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The Oxychlorides of Mercury. Equilibrium in the System: Mercuric Chloride, Yellow Mercuric Oxide and Water at 35°C.

By

Shigeru Toda.

(Received May 24, 1920.)

The oxychlorides of mercury have been studied by many investigators and a series of the compounds have been described.[1] The following is a summary of those oxychlorides found in the literature:

Compounds.	Observers.
$2HgCl_2.HgO$	Roucher, Thuemmel, Arctowski, Schoch.
$HgCl_2.HgO$	Roucher, Thuemmel, Tarugi.
$HgCl_22.HgO$	Millon, Roucher (in 3 modifications), Thuemmel, Arctowski, Tarugi, Volhard, Schoch (in 3 modifications).
$HgCl_2.2HgO.\frac{1}{2}H_2O$	Ray.
$BgCl_2\ 3HgO$	Millon, Roucher (in 3 modifications),

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1 E. Millon, Ann. chim. phys., (3) **18**, 372 (1846);
C. Roucher, ibid, (3) **27**, 353 (1849); J. pr. Chem., **49**, 363 (1850);
K. Thuemmel, Arch. Pharm., **227**, 589 (1886);
M. G. André, C. R., **104**, 431 (1887);
H. Arctowski, Z. anorg. Chem., **9**, 176 (1895);
J. Volhard, Ann. Chem., **255**, 252 (1889);
P. C. Ray, Proc. Chem. Soc., **15**, 103 (1899); Ann. Chem., **316**, 255 (1901);
N. Tarugi, Chem. Centralbl., **72 II**, 1147 (1901) from Gaz. chim. ital., **31 II**., 313;
E. P. Schoch, Amer. Chem. J., **29**, 319 (1903).

	Andre, Tarugi, Schoch (in 3 modifications).
$2HgCl_2.3HgO$	André, Arctowski.
$HgCl_2.4HgO$	Millon, Roucher (in 4 modifications), Thuemmel, Arctowski, Schoch (in 3 modifications).
$HgCl_2.5HgO$	Roucher.
$HgCl_2.6HgO$	Roucher (in 2 modifications).
$HgCl_2.6HgO\ H_2O$	Roucher.

Tarugi explained all the oxychlorides except the three compounds, $HgCl_2.3HgO$, $HgCl_2.2HgO$, and $HgCl_2.HgO$, to be mixtures of indefinite chemical composition.

As seen from the above cited literature, a systematic investigation of the oxychlorides of mercury was desirable and on the suggestion of Prof. Y. Osaka, the writer took up the problem to study it from the standpoint of the phase rule, taking mercuric chloride, yellow mercuric oxide and water as the components.

The materials were prepared as follows: Mercuric chloride of Jap. Pharm. was purified by thrice recrystallisation, and mercuric oxide was prepared by the methods given in L. Vanino's Handbuch.[1]

The experiments were carried out in the following way: Mixtures of salts in different proportions were put each in an Erlenmeyer flask of a capacity of about 30 c.c. with a well ground stopper, which was made to rotate in a thermostat at 35°C. for about three days and nights. When equilibrium was attained, the flask was allowed to stand still in the same thermostat until the suspended matter had completely subsided, then a proper portion of the mother liquor was taken out by a pipette, through a short glass tube filled with purified cotton and attached to the pipette by a rubber tubing, to a weighing bottle and subjected to analysis.

To prepare the residue for analysis, it was pressed down between folded filter paper to remove the adhering mother liquor as much as possible, then a part of it, previously weighed, was redissolved in water with the addition of the necessary quantity of nitric acid. The solution thus obtained was diluted to a definite volume and divided into proper portions, for analysis.

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[1] Handbuch der preparativen Chemie, I, 461.

The methods of analysis used were as follows: Hydrogen sulphide solution which was absolutely free from chlorine was added to the sample to remove the mercury. It was gently boiled until the excess of hydrogen sulphide was expelled, then the precipitate was filtered and washed five times with hot water. The filtrate was used for the determination of chlorine according to Volhard's method, improved by V. Rothmund and A. Burgstaller.

Mercury was precipitated as mercuric sulphide with ammonium sulphide, prepared as directed in Vanino's Handbuch.[1] It was collected in a Gooch crucible, dried at 110°C. and weighed.

Results.

The results are given in the following table:—

TABLE I.

	Solution.		Residue.[2]	
No.	$HgCl_2$ in gram percentage.	HgO in gram percentage.	$HgCl_2$ in gram percentage.	HgO in gram percentage.
1	8·58	—	—	—
2	8·72	0·14	96·82	1·65
3	8·68	0·07	76·88	16·50
4	8·69	0·10	60·55	30·67
5	8·81	0·03	53·07	37·68
6	8·70	0·11	40·34	50.03
7	8·69	0·10	37·01	55·19
8	4·39	0·09	36·13	58·41
9	3·42	0·06	37·01	55·19
10	0·66	0·02	36·13	58·42
11	0·66	0·02	30·14	57·70
12	0·61	0·02	22·28	59·20
13	0·23	0·03	21·68	61·07
14	0·20	0·06	20·84	59·46
15	0·13	0·04	16·55	55·09
16	0·07	0·04	16·40	50·05
17	0·05	0·03	10·36	69·80
18	0·05	0·04	6·48	77·24

1 Loc. cit., 337.

2 The residue was slightly wet with the mother liquor.

19	0·04	0·04	1·10	83·26
20	0·01	0·03	0·35	90·04
21	—	0·001	—	—

The following table was calculated from the last, using the following formula to represent the compositions of the solutions and residues:

$$100m\ H_2O\ x HgCl_2\ (100\text{-}x)HgO$$

and in the table, a function of m, $N = \frac{100m}{100+m}$, was calculated to represent the amount of water.

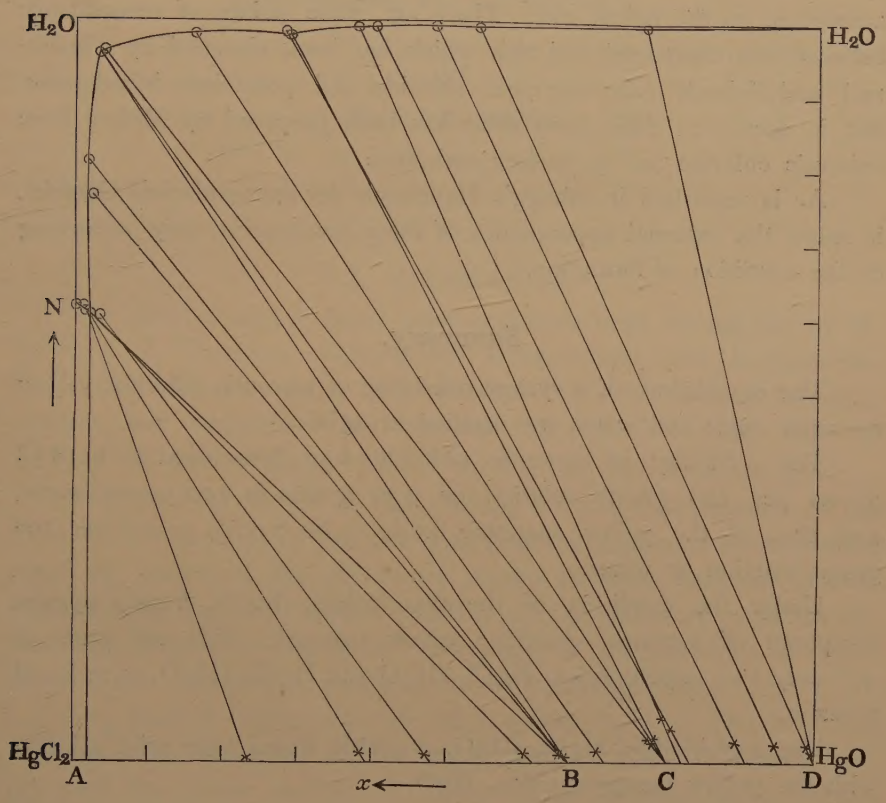
TABLE 2.

	Solution.		Residue.		
No.	N	x	N	x	Formula of the residue found graphically.
1	61·63	100·00	—	—	$HgCl_2$
2	60·69	97·99	0·23	97·92	$HgCl_2 + HgCl_2.2HgO$
3	61·50	99·00	0·69	76·83	,, ,,
4	60·98	98·64	1·32	61.16	,, ,,
5	60·06	96·58	1·37	52·89	,, ,,
6	60·88	98·50	1·39	39·15	,, ,,
7	60·94	98·64	1·09	34·86	$HgCl.2HgO$
8	76·18	97·53	0·75	33·03	,,
9	80·63	98·00	1·10	34·86	,,
10	95·62	96·81	0·74	33·05	,,
11	95·61	96·78	1·76	29·42	$HgCl_2.2HgO + HgCl_2.4HgO$
12	95·92	96·23	2·81	23·10	$HgCl_2.4HgO$
13	98·21	84·10	2·64	22·07	,,
14	98·20	71·34	3·02	21·86	,,
15	98·81	72·03	4·76	19·34	$HgCl_24HgO + HgO$
16	99·22	62·24	6·01	20·72	,, ,,
17	99·42	59·92	2·96	10·58	,, ,,
18	99·38	51·81	2·33	6·27	,, ,,
19	99·45	46·08	2·19	1·05	HgO
20	99·67	23·31	1·26	0·31	,,
21	100·00	0·00	—	—	,,

The above results are graphically shown in Fig. 1, in a square

diagram, measuring water (N) on the vertical side and molarpercentages of the chloride (x) on the horizontal side.

Fig. 1.



From this figure, it may be easily seen that we have only two definite oxychlorides represented by the points B and C, corresponding to the formula, $HgCl_2.2HgO$ and $HgCl_2.4HgO$, respectively. The oxychloride, $HgCl_2.4HgO$, forms probably some solid solution with the oxide, but the data are insufficient to say much about it.[1]

Now, some remarks will be made above the external appearance of the two compounds, obtained in the present investigation.

The oxychloride, $HgCl_2 2HgO$, is dark purple-reddish, needle shaped crystals. Judged from the color tone it may be the same

1 The writer had only a limited period of time for the investigation and could not work out more completely.

compound as has been prepared by Volhard[1] from mercuric chloride and sodium acetate or by Millon[2], Thuemmel[3] and Schoch[4] from mercuric chloride and potassium carbonate.

The oxychloride, $HgCl_2.4HgO$, is a brownish yellow substance, amorphous to the naked eye. There are some points of resemblance between this compound and that which has been obtained by Thuemmel[4] and Schoch[5] from mercuric chloride and potassium bicarbonate, but it seems to differ from what has been prepared by Millon[2] from mercuric chloride and potassium carbonate.

As is remarked in Abegg's Handbuch der anorganischen Chemie[5], it seems the external appearances of these compounds vary according to the condition of formation.

Summary.

The equilibrium of a system consisting of mercuric chloride, yellow mercuric oxide and water was studied at 35°C.

The solubility of mercuric chloride was determined to be 8·58 grams per 100 grams solution or 9·39 grams in 100 grams water, and that of the yellow mercuric oxide to be 0·0014 grams per 100 grams solution or water.

Under the condition of the experiments, that is, from a system composed of mercuric chloride, yellow mercuric oxide and water at 35° only two oxychlorides, $HgCl_2.2HgO$ and $HgCl_2.4HgO$, were found to exist.

The oxychloride, $HgCl_2.4HgO$, probably forms some solid solution with the yellow mercuric oxide, HgO.

In conclusion the writer wishes to express his sincere thanks to Prof. Y. Osaka for his interest and advice throughout the experiment.

1, 2, 3, 4 Loc. cit.

5 Vol. II, 2, p. 623.

On the Evidence of the Existence of Isotopes of Chlorine.

By

Matakichi Ishino.

(Received July 22, 1920.)

§ 1. Introduction.

The positive rays of many substances have been investigated by W. Wien, J. J. Thomson, Retschinsky, Königsberger and Kutschenski, Stark, Bärwald and others. J. J. Thomson[1] used the crossed deflection method, and obtained many important results as to the value of $\frac{m}{e}$ and the nature of the charged particles in a positive ray tube.

The great advantage of this method for the determination of the mass of particles lies in the fact first, that the method does not depend upon the purity of the substances used; secondly, that the method requires only a very minute quantity of the substance; and thirdly, that the method furnishes the knowledge of the existence of some intermediate states of a substance in the discharge-bulb.

The positive rays of chlorine were studied by J. J. Thomson, and he found the existence of the types Cl^+, Cl^-, Cl^{++}. Stark also observed the same carriers by means of the Doppler effect. When about four years ago the author worked on this gas at Cambridge, the line corresponding to Cl^+ appeared as if its breadth was somewhat wide. But owing to pressure of work, the author postponed further research in this field. The aim of the present investigation is to attack the above important problem of the positive rays of chlorine atoms.

§ 2. The Experimental Details.

The apparatus, which was used for the analysis of the positive rays of chlorine, was constructed on the principle of Thomson's crossed deflection method. The positive-ray particles resolved by the electrostatic

1 "Rays of Positive Electricity and their Application to Chemical Analysis" Longmans, Green and Co, London, 1913.

and magnetic fields were photographed on a plate placed at right angles to the direction of the ray. In order to secure the exact coincidence of the direction of the electrostatic and magnetic fields, two soft-iron blocks with parallel plane faces were used at the same time, as the electrodes and the magnetic poles. The diameter of the cathode-canal used was about 0.1 m.m. The pumping of the apparatus was carried out by a Gaede molecular pump with his ordinary mercury pump as an auxiliary. After many preliminary experiments, the author found that the intensity and sharpness of the lines on the photographic plate depend remarkably upon the pressure of the camera-side of the apparatus. This is obviously due to the absorption and scattering of the positive rays by the residual gas-molecules in the camera-side. Therefore, it is of primary importance in this work to produce extremely high vacua. Every part of the apparatus was washed thoroughly with suitable reagents and boiled in water for several hours, and finally thoroughly dried. This was to remove any volatile substance remaining in adherence to the walls of the apparatus. After properly setting the apparatus, the whole was exhausted with the pumps mentioned above, and then sufficiently heated. The exhaustion was continued for two or three days after the photographic plate was placed in the camera. This was found to be very necessary, because otherwise some gases or vapours would contaminate the surface of the film. The vacuum attained in this way was about 0.00001 m.m. of mercury.

The resolving power of the apparatus may be, of course, increased by raising the intensity of the magnetic field. If this be done, however, the intensity of the lines necessarily falls off. Therefore in order to obtain fine lines with great resolution, a very sensitive photographic plate for the positive rays was necessary. The author has tried the various photographic plates available, among which the Schumann plates from Adam Hilger were found to bc very good. The author has newly prepared Schumann plates with the kind help of Assist. Prof. Miyata. The prescription of the plate was the same as that of Schumann,[1] except for a certain modification to render the film as thin as possible, and to contain as much silver as possible. This plate prepared thus was found very sensitive, so that the time of exposure to to the positive rays was reduced to only a minute or a half minute to get measurable fine lines.

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[1] Ann. Physik, 5, 349 (1901).

The chlorine gas to be studied was prepared by electrolysis of hydrochloric acid, dried with Cl_2Ca and P_2O_5, and introduced into the discharge-bulb through fine capillary tubes. The gas was also obtained by means of the bombardment of the powder of natrium chloride with cathode rays, the salt being introduced in a side-tube connected with the discharge-bulb.

§ 3. Results.

The photographs of the broadened line of chlorine were repeatedly taken under different conditions. When the magnetic field was sufficiently intense, and the pressure in the camera was as extremely low as 0.00001 m.m. the broadened line under the consideration was separated into two lines. The separation occurred equally for the positive carriers and the negative ones. The photographs are shown in the accompanying plate, the time of exposure of which was about one minute, and the pressure in the discharge-bulb about 0.001 m.m. The measurement of the value of m/e for the above two lines proved to be **34** and **36**, compared with that of the hydrogen atom. The intensities of the two lines appear not to be equal, that of the line 34 being much the fainter.

In addition to these lines a line 37 appeared on the positive side, i.e. the side where the positive carriers impinge.

The line 36 has the second bead midway between the first bead and the vertical line, i.e. the line corresponding to the deflection due to the magnetic field alone, and another line 18 is seen on the plate. But the second bead of the line 34 is so faint that it is only observable on the original plate. The second beads of the lines 34 and 36 are also seen on the negative side of the plate.

In some plates the third bead is often observed at a distance one third of that of the first bead from the vertical line. Considering this third bead we may expect the occurrence of a line $36/3=12$, and in fact, an intense line 12 is seen on the plate. But since this line just coincides in value with the line of the carbon atom, it is not possible to tell whether the line is due to the atom corresponding to the third bead of the line 36, or the carbon-atom.

J. J. Thomson was not able to find any case in which a molecule of either an elementary or compound gas carries multiple charges; and he had never found molecules with a negative charge, though molecules with the positive charge are quite common. Considering

these empirical facts, it is highly possible that the lines 34 and 36 are due to elementary atoms.

Now these two lines appeared only when the chlorine gas was introduced into the discharge-bulb, and consequently it may be concluded that these two lines are due to chlorine atoms. But a question arises as to the nature of the line 34, because this line may be due to H_2O_2. To test this point, a new apparatus was constructed using fresh materials. The gas H_2O_2 was prepared by adding concentrate sulphuric acid to barium peroxide, and was then introduced into the discharge-bulb. With this gas, the author could not observe any trace of the line 34 and 36 on the photographic plate.

It is also possible to consider the line 34 as due to H_2S (=34). In a side-tube connected with the discharge-bulb, molten SO_2HNa was introduced. On heating or bombardment with cathode rays this substance evolved H_2S gas. Many photographs were now taken of this gas by using a newly constructed apparatus, but the suspected line did not make any appearance at all.

So far as the experiments are concerned the author is inclined to think that the line 34 and 36 are both due to chlorine atoms.

If this conclusion is correct, then we must accept the existence of the isotopes of the element chlorine. Let the atoms of these isotopes be denoted by the symbols $Cl_I=34$, and $Cl_{II}=36$.

Then the ordinary chlorine of the atomic weight 35.45 would be a mixture of $x.Cl_I+y.Cl_{II}$, where x and y represent the relative coefficients of the amount of isotopes.

The line 37 is clearly due to the hydride of Cl_{II}, i.e. HCl_{II}. Another hydride HCl_I (=35) is not seen on the plate, but the broadening of the line 37 seems to show the existence of such a hydride.

Finally it is to be noticed that in addition to a number of the atoms of chlorine with negative charge, there exists also the atoms with positive charge. This fact is against the expectation of some scientists, who thought that positive ions of chlorine can hardly exist in a discharge-bulb, because chlorine is a very strong electro-negative element.

§ 4. Discussion.

It is rather remarkable that the atomic weights of the lighter elements up to cobalt are approximately whole numbers, with just a

few exceptions, Ne, Mg, Si, and Cl. The same facts occur also in the case of very heavy radioactive elements. Such facts are much too conspicuous to be considered merely accidental.

According to Rutherford's atom-model, the mass of an atom mainly resides in the positive nncleus, which is surrounded by electrons rotating in certain orbits. The study of radioactive phenomenon shows that a positive nucleus of an atom has a complex structure, and consists probably of the positive nuclei of helium and of hydrogen, and some cementing electrons. With this conception we can understand to some extent why the whole-number rule is held for the atomic weights.

The atomic weights of the majority of the moderately heavier elements and a few elements among the lighter ones above mentioned deviate remarkably from the whole-number. This deviation is apparently contradictory to such a nuclear structure as given above. It is therefore very important for the problem of atomic structure, to inquire into the cause of this deviation from the whole-number.

The cause of the deviation may be ascribed to the existence of isotopes. Suppose now that there are isotopes to an element, and an ordinary element is a mixture of such isotopes. According to this view the atomic weight of an element is only the average of the atomic weights of the constituent atoms. Hence even if the whole-number rule holds good for each atom, the average atomic weight may be generally different from the whole number.

The deviation of the atomic weight of chlorine is, as is well known, the greatest among the ligher elements. Judging from the results of the present study, the large deviation in the case of chlorine, can be explained by the existence of the isotopes.

It is here dcsirable to notice that this investigation was carried out in Sept. of last year. But owing to the pressure of work in the Institute and the author's illness, the publication was greatly delayed. Meanwhile Mr. Aston's letter was published in *Nature*[1], stating that he had found isotopes of chlorine by using a new method of positive-ray spectrography, the atomic weights obtained being 35 and 37, respectively.

In conclusion, the author wishes to express his indebtedness to Professor T. Mizuno for the interest he has taken in this investigation. The author's thanks are also due to Mr. Arakatsu for his useful help.

1 Aston, Nature, Jan. 1920.

Fig. 1

$\alpha = 34 \ldots Cl_I$
$\beta = 36 \ldots Cl_{II}$
$\gamma = 72 \ldots Cl_2$

Fig. 2

$\varepsilon = 37 \ldots Cl_{II}$ H.

Fig. 3

The second and the third beads of chlorine-atom

A Study of the Reciprocal Salt Pairs: $Na_2Cl_2+MgSO_4 \rightleftarrows Na_2SO_4+MgCl_2$ at 25°C.

By

Shirow Takegami.

(Received August 18, 1920)

Various heterogeneous equilibria in systems consisting of water and almost all possible combinations of the chlorides and sulphates of sodium, potassium, magnesium, and calcium were studied by J. H. van't Hoff[1] and his co-workers during the years 1897–1908. Their work had in view the explanation of the genesis of the oceanic salt deposits in Stussfurt and other places. Up to this present, however, there has been no systematic study of those reciprocal salt pairs above-named. We have some data for some parts of this system, but some of them are not sufficiently exact. Therefore the author, on the suggestion of Prof. Y. Osaka, took up the study of the equilibrium of the system at 25°C. from the standpoint of the phase rule.

About two months ago when the present work was nearly completed, an article on the same subject by W. C. Blasdale[2] came to the author's notice, but since his results are not in agreement with the author's at several points, he continued his work, which seemed not to be superfluous. The results are given in this article.

Materials: Sodium sulphate, magnesium sulphate, and magnesium chloride were purified by thrice recrystallisation from commercial pure salts, as $Na_2SO_4 . 10H_2O$, $MgSO_4 . 7H_2O$, and $MgCl_2 . 6H_2O$ respect-

1 J. H. van't Hoff: Untersuchungen über die Bildungsverhältnisse der ozeanischen Salzablagerungen. Leipzig Akademische Verlagsgesellschaft, 1912; J. Chem. Soc. Abst. (1898), ii, 564, ff. from Sitzungsber. K. Akad. Wiss. Berlin.

2 J. Ind. Eng. Chem. **2**, 164 (1920).

ively, and sodium chloride was prepared by precipitation from a saturated solution of commercial pure salt by hydrochloric acid gas.

Methods of experiments: All the experiments were divided into three parts, namely,

1. Measurement of solubilities of four single salts.
2. Study of equilibria between two salts which have a common ion.
3. Study of the equilibria among three salts, namely, that of the reciprocal salt pairs.

The experiments were carried out in the following way: Mixtures of salts in different proportions were put each in an Erlenmeyer flask of a capacity of about 30 c.c. which was made to rotate in a thermostat at 25·0°C. for at least twenty-four hours. When equilibrium was attained, the flask was allowed to stand for a while in the same thermostat until the suspended matter had settled. Then about 10 c.c of the solution were sacked up by a pipette through a cotton filter into a weighing bottle, and subjected to analysis. The residue which had been pressed between a porous plate and folded filter paper, was redissolved in water to a definite volume, for analysis. The residue taken for analysis was sometimes still wet with some mother liquor, but naturally it had no influence over the determination of the nature of the residue.

Magnesium and sulphate radicals were determined as magnesium pyrophosphate and barium sulphate respectively, and chlorine by titration with a 1/20-normal silver nitrate solution. Sodium was estimated by difference.

1. *The solubilities of single salts:* The solubilities of single salts, found in the present investigation, are given together with the data found in literature as follows (Grams anhydrous salt per 100 grams of solution):[1]

a. *Sodium chloride.*

1. 26·52
2. 26·46 } 26·49 (Takegami)

26·47 (Osaka)[2]
26·52 (Mulder)[3]
26·30 (Kopp)[3]

[1] Here and in the following pages, the data quoted from the literature were recalculated, when necessary, to make them comparable with the author's.
[2] J. Tokyo Chem. Soc., **29**, 116 (1908).
[3] Landolt, Bernstein, Meyerhoffer's Tabellen, p. 556.

b. *Sodium sulphate.*

1. 21·33
2. 21·55 } 21·54 (Takegami)
3. 21·53 }

21·9 (Mulder)[1]

c. *Magnesium chloride.*

1. 35·90 } 35·86 (Takegami)
2. 35·81 }

36·1 (Löwenherz)[2]

36·2 (van't Hoff and Meyerhoffer)[3]

d. *Magnesium sulphate.*

1. 26·59 } 26·68 (Takegami)
2. 26·77 }

28·2 (Mulder)[4]

25·9 (Löwenherz)[2]

27·9 (van't Hoff)[3]

2. *Equilibria between two salts which have a common ion.*

a. *Sodium chloride and sodium sulphate.*

The results of the determination of solubility are given in the following table:—

TABLE I.

Composition of solution in gram percentages.				Composition of residue in gram percentages.		
No.	Na_2Cl_2	Na_2SO_4	H_2O	Na_2Cl_2	Na_2SO_4	H_2O
1	26·49	...	73·51	...	...	...
2	24·57	3·00	72·43	90·92	0·14	8·94
3	22·98	6·80	70·22	49·54	35·90	14·56
4	20·47	8·60	70·93	5·04	79·65	15·31
5	18·95	10·12	70·93	3·65	81·05	15·30
6	13·06	15·60	71·34	4·13	78·59	17·28
7	13·07	15·60	71·33	1·54	90·61	7·85
8	13·61	15·18	71·21	2·64	45·63	51·73
9	9·74	15·65	74·61	3·68	33·37	62·95
10	4·21	18·25	77·54	1·12	37·51	61·37
11	...	21·54	78·46	...	...	...

1 Seidell: Solubilities of inorganic and organic substances, p. 311.
2 Zs. physik. Chem., **13**, 459 (1894).
3 Ozeanische Salzablagerungen, p. 42.
4 Loc. cit.

The following table was recalculated from the last one by representing the compositions of solutions and residues by the formula:

$$100mH_2O.xNa_2Cl_2.(100-x)Na_2SO_4,$$

where x denotes the molar percentage of Na_2Cl_2 and m the number of moles of water to one mole of salt.

TABLE 2.

No.	Solution		Residue		
	x	m	x	m	Solid phase
1	100·00	18·02	...	...	Na_2Cl_2
2	90·88	17·40	99·87	0·64	„
3	80·40	15·96	62·65	1·20	Na_2Cl_2; Na_2SO_4
4	74·32	16·73	7·14	1·40	Na_2SO_4
5	69·42	16·89	5·19	1·41	„
6	50·44	17·90	6·00	1·63	„
7	50·44	17·90	2·02	0·67	„
8	51·31	18·03	6·57	8·38	Na_2SO_4; $Na_2SO_4 \cdot 10H_2O$
9	43·06	21·42	11·82	13·13	$Na_2SO_4 \cdot 10H_2O$
10	21·91	26·20	3·50	12·46	„
11	0·00	28·51	...	...	„

From the dada on this table, we obtain Fig. 1.

From Fig. 1, it may be seen that the decahydrate of sodium sulphate is dehydrated to the anhydrous form when the amount of sodium chloride in the saturated solution of sodium sulphate is increased to some definite degree. And there is no formation of any double salt between them.

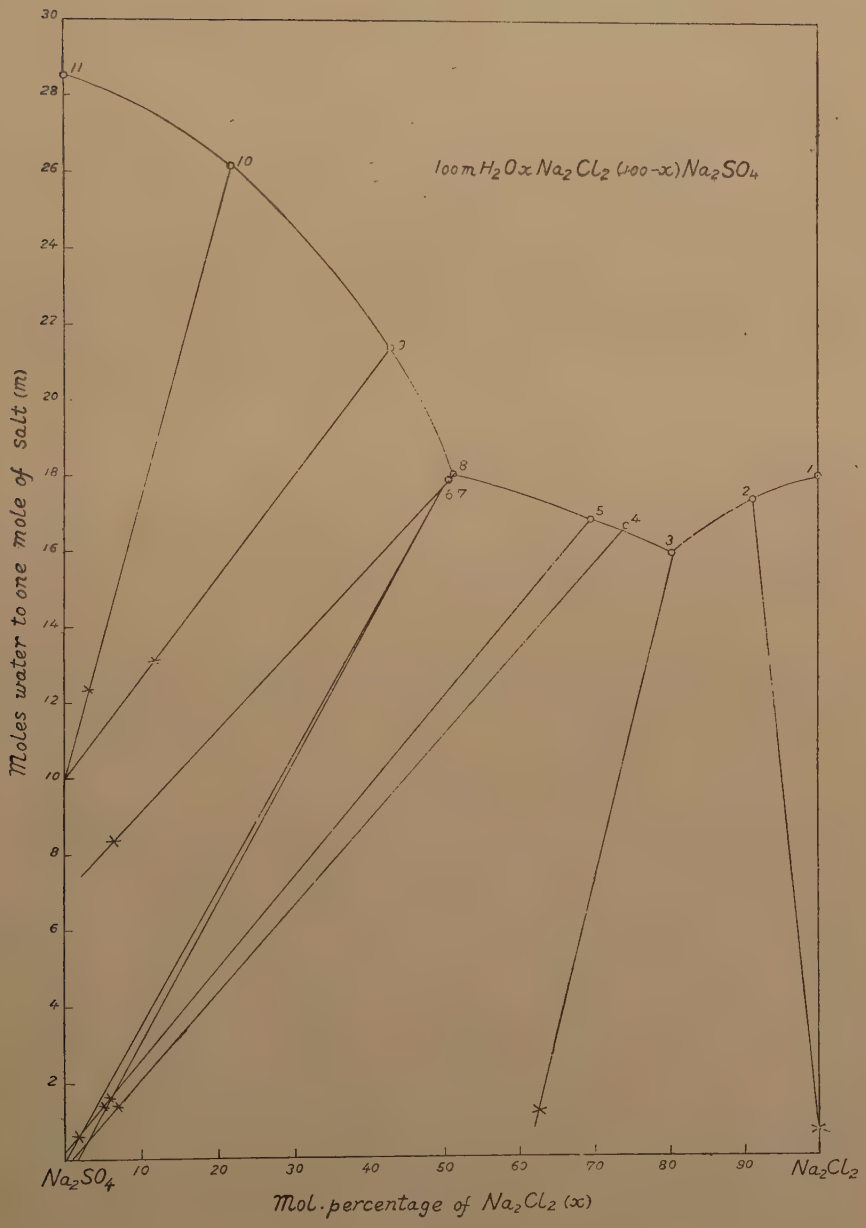
About this equilibrium, though a part of it has been reported by van't Hoff,[1] it seems, there has been no complete investigation except the most recent studies of Blasdale.[2] The values found by these two authors are in fair agreement with those found in the present investigation.

The solution, saturated with sodium chloride and sodium sulphate, corresponds to the point 3, of which

1 van't Hoff: Ozeanische Salzablagerungen, p. 73.

2 Loc. cit.

Fig. 1.


100 m H_2O x Na_2Cl_2 (100-x) Na_2SO_4
Moles water to one mole of salt (m)
Mol. percentage of Na_2Cl_2 (x)
Na_2SO_4
Na_2Cl_2
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
10
20
30
40
50
60
70
80
90
1
2
3
4
5
6
7
8
9
10
11

$$m = 15{\cdot}96 \quad \text{and} \quad x = 80{\cdot}40,$$

while according to the previous investigatiors, they are

$$m = 16{\cdot}0, \quad x = 81{\cdot}6 \quad \text{(van't Hoff)}$$
$$m = 16{\cdot}12, \quad x = 79{\cdot}93 \quad \text{(Blasdale)}$$

The coordinates of the points 8, which represents the solution saturated with anhydrous and decahydrated sodium sulphate are

$$m = 18{\cdot}03, \qquad x = 51{\cdot}31$$

while those found by Blasdale are

$$m = 17{\cdot}70, \qquad x = 51{\cdot}34$$

b. Sodium chloride and magnesium chloride.

The equilibrium of this system is very simple as shown in Fig. 2, Tables 3, and 4, as there is no formation of any double salt nor change of water of crystallisation in the salts.

TABLE 3.

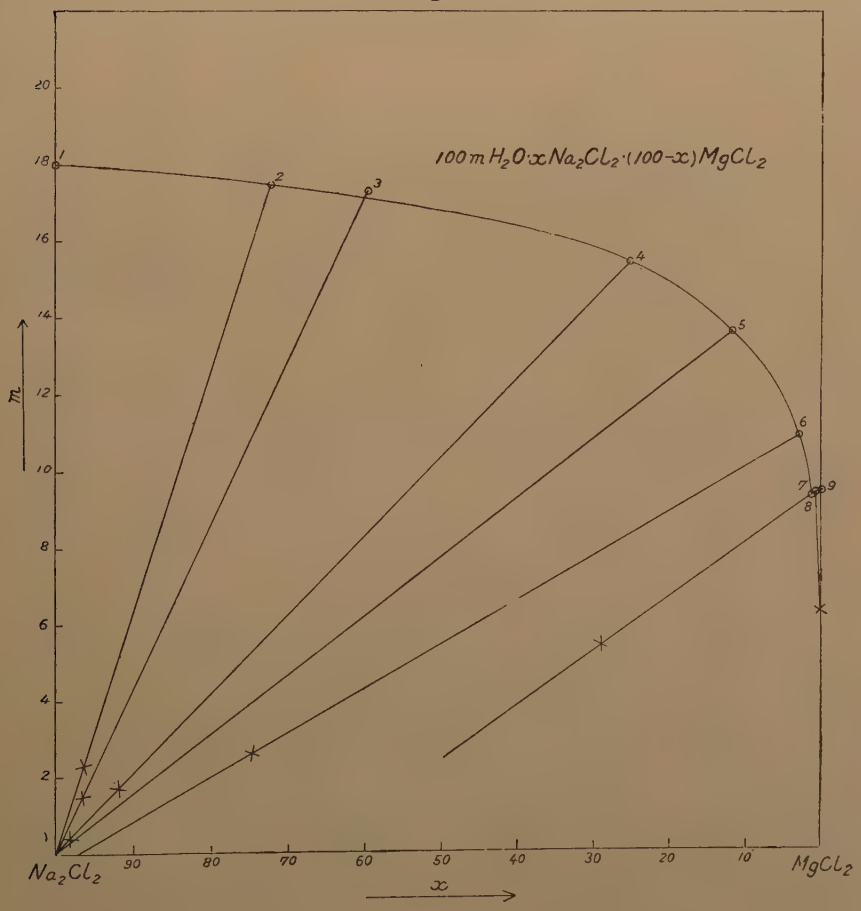
No.	Composition of solution in gram percentages			Composition of residue in gram percentages		
	Na_2Cl_2	$MgCl_2$	H_2O	Ma_2Cl_2	$MgCl_2$	H_2O
1	26·49	...	73·51	...	...	...
2	19·77	6·24	73·99	71·44	2·24	26·32
3	16·62	9·15	74·23	78·41	2·52	19·07
4	7·80	18·79	73·41	73·15	5·48	21·37
5	4.11	24·40	71·49	82·53	11·73	5·74
6	1·12	31·65	67·23	55·20	15·27	29·53
7	0·48	35·68	63 84	16·28	35·16	48·56
8	0·21	35·73	64·06	0 00	45·55	54·45
9	...	35·86	64·14	...	...	...

TABLE 4.

$100mH_2O{\cdot}xNa_2Cl_2{\cdot}(100-x)MgCl_2$

No.	Solution		Residue		
	x	m	x	m	Solid phase
1	100·00	18·02	...	...	Na_2Cl_2
2	71·95	17·49	96·11	2·30	„
3	59·50	17·26	96·19	1·52	„
4	25·15	15·38	91·56	1·72	„
5	12·00	13·59	98·27	0·44	„
6	2·79	10·86	74·54	2·59	„
7	1·08	9·32	27·95	5·42	Na_2Cl_2; $MgCl_2.6H_2O$
8	0·27	9·40	0·00	6·29	$MgCl_2.6H_2O$
9	0·00	9·41	...	...	„

Fig. 2.



The composition of the solution saturated with the two salts, represented by the point 7 in Fig. 2 is

$$x=1\cdot08 \quad \text{and} \quad m=9\cdot32.$$

The corresponding values found by van't Hoff are

$$x=2\cdot3 \quad \text{and} \quad m=9\cdot4.$$

According to Blasdale, however, the solubility of sodium chloride in the saturated solution of magnesium chloride is negligibly slight, so that it may be represented by

$$x=0\cdot00 \quad \text{and} \quad m=9\cdot63$$

As seen from the above statement, the solubility of sodium chloride in the saturated solution of magnesium chloride is much less than that found by van't Hoff but not so trifling as Blasdale has observed.

c. Magnesium sulphate and sodium sulphate.

Into the only double salt, astrakanite, $Na_2Mg(SO_4)_2.4H_2O$, which these two sulphates form, there are many investigations,[1] but no systematic study of the equilibrium of this system at 25°C. seems to have been published until the work of Blasdale appeared. The results of the author are represented in Table 5, 6, and Fig 3.

TABLE 5.

No.	Composition of solution in gram percentages			Composition of residue in gram percentages		
	$MgSO_4$	Na_2SO_4	H_2O	$MgSO_4$	Na_2SO_4	H_2O
1	26·68	...	73·32	...	...	...
2	23·77	6·69	69·54	39·35	2·52	58·13
3	20·06	10·80	67·14	37·85	3·18	58·97
4	19·84	26·54	63·62	36·29	7·08	56·63
5	21·60	12·45	65·95	33·59	24·91	41·50
6	19·46	14·13	66·41	30·96	32·75	36·29
7	18·28	15·89	65·83	29·40	26·58	44·02

1 J. H. van't Hoff and Ch. M. van Deventer; Zs. physik. Chem., **1**, 170 (1887); **3**, 337 (1889); Ber., **19**, 2144; H. W. B. Roozeboom: Zs. physik. Chem., **2**. 518 (1888).

8	16·31	18·22	65 47	28·25	31·28	40·47
9	16·14	18·16	65·70	28·68	32·21	39·11
10	14·14	20·50	65·36	27·85	34·00	38·15
11	15·63	18·63	65·74	12·56	37·59	49·85
12	17·67	18·16	64·17	6·32	34·68	59·00
13	10·93	19·17	69·90	3·75	35·97	60·31
14	10·78	18 85	70·37	4·54	33·28	62·18
15	3·34	20·88	75·78	0·55	41·40	58·05
16	...	21·54	78·46	...	...	...

TABLE 6.

$100mH_2O \cdot xMgSO_4 \cdot (100-x)Na_2SO_4$

No.	Solution		Residue		
	x	m	x	m	Solid phase
1	100·00	18·31	...	...	$MgSO_4.7H_2O$
2	81·79	15·74	94·80	9·32	„
3	70·68	14·35	93·38	9·69	„
4	58·70	12·54	85 86	8·93	„
5	67·28	13·69	61·51	5·06	$MgSO_4.7H_2O$; Astrakanite
6	62·01	14·09	52·83	4·13	Astrakanite
7	57·70	13·84	51·73	5·71	„
8	51·49	13·77	51·70	4·93	„
9	51·30	13·91	51·30	4·66	„
10	44·98	13·85	49·26	4·49	„
11	49·86	13·97	28 35	7·00	Astrakanite; $Na_2SO_4.10H_2O$
12	53·55	12·95	17·76	11·05	$Na_2SO_4.10H_2O$
13	40·31	17·18	11·00	11·79	„
14	40·41	17·57	13 92	12·70	„
15	15·95	24·08	1·55	10·90	„
16	0·00	28·51	...	...	„

The transition points, 5 and 11, as found by Blasdale, are respectively :

$x=65{\cdot}77, \quad m=13{\cdot}71$ and
$x=52{\cdot}48, \quad m=13{\cdot}83$

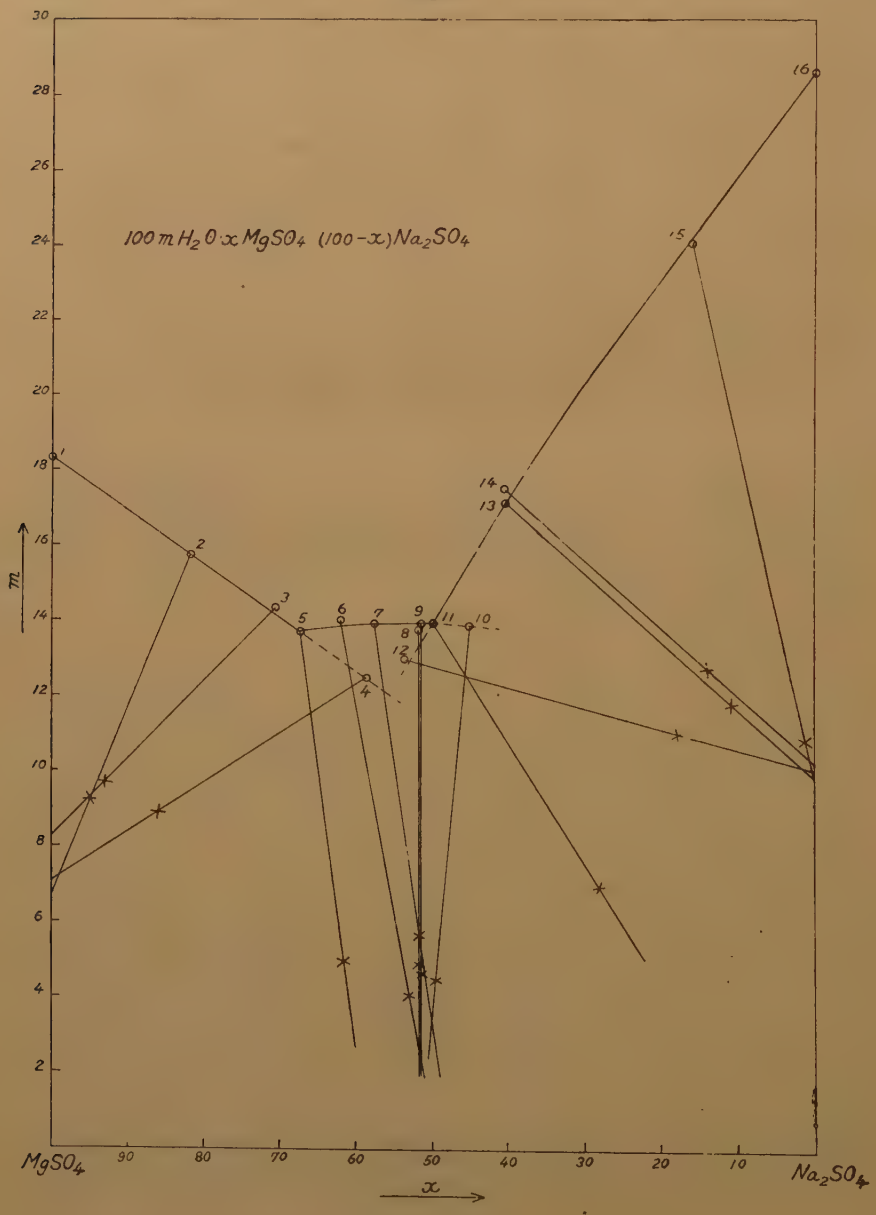
against the author's values

$x=67{\cdot}28, \quad m=13{\cdot}69$;
$x=49{\cdot}86, \quad m=13{\cdot}97$.

As may be seen, there is some difference between them, but it does not much matter for the present purpose.

The data marked with an * refer to labile equilibrium, and that part is represented in the diagram with dotted lines.

Fig. 3.



d. Magnesium chloride and magnesium sulphate.

Of the equilibria of the four systems each of two salts with a common iron, those of the three already mentioned do not much differ in essential points from those found by previous investigators.

Now, as to the fourth system, the opinions of the previous observers are divided; and as the equilibrium state of this system has a great influence upon that of the reciprocal salt pairs, it is the most important and the most interesting of the four ternary systems.

According to Löwenherz,[1] the first systematic investigator of this system, the solubility curve in this system consists of three branches in consequence of the change of water of crystallisation of magnesium sulphate from hepta to hexa. He determined the compositions of the solutions which have the two salts, $MgSO_47.H_2O$ and $MgSO_4.6H_2O$, and $MgSO_4.6H_2O$ and $MgCl_2.6H_2O$, as residue respectively to be

$$x=83,\quad m=11{\cdot}3 \qquad \text{and} \qquad x=88,\quad m=8{\cdot}5.$$

According to van't Hoff,[2] however, there exist two more hydrates, namely, penta and tetra, and his results are as follows:

x	m	Residue.
83·0	11·4	$MgSO_4.7H_2O$; $MgSO_4.6H_2O$.
90·4	10·7	$MgSO_4.6H_2O$; $MgSO_4.5H_2O$.
92·2	10·4	$MgSO_4.5H_2O$; $MgSO_4.4H_2O$.
94·9	9·4	$MgSO_4.5H_2O$; $MgCl_2.6H_2O$.

The Blasdale's results are very near to those of Löwenherz, and no investigations have been undertaken about the penta and tetra hydrates of magnesium sulphate. His data are as follows:

x	m	Residue.
88·98	11·55	$MgSO_4.7H_2O$; $MgSO_4.6H_2O$.
93·65	9·30	$MgSO_4.6H_2O$; $Mg.Cl_2.6H_2O$;

The author's results are represented in Tables 7, 8, and Figs. 4 and 5.

1 Zs. physik. Chem., **13.** 459, (1894).

2 van't Hoff: Ozeanische Salzablagerungen p. 71, Ber. Berl. Akad., 1898, 487.

TABLE 7.

No.	Composition of solution in gram percentages			Composition of residue in gram percentages		
	$MgCl_2$	$MgSO_4$	H_2O	$MgCl_2$	$MgSO_4$	H_2O
1	...	26·68	70·32	...	...	...
2	1·62	24·43	73·95	0·52	40·38	59·10
3	5·31	19·63	70·06	—	—	—
4	9·42	14·89	75·69	3·13	36·81	60·06
5	10·51	14·02	75·47	3·18	37·89	58·93
6	14·05	10·68	75·27	4·78	35·77	59·45
7	14·77	11·c8	74·15	4·60	37·35	58·05
8	16·22	10·14	73·64	4·76	37·17	58·07
9	23·53	5·44	71·03	5·11	39·21	55·68
10	26·06	5·02	68·92	7·44	37·83	54·73
11	26·36	4·90	68·74	9·22	35·80	54·98
12	27 84	4·29	67·87	3·35	45·66	50·99
13	28·21	4·35	67·44	11·55	32·59	55·86
14	28·72	4·14	67·14	10·63	34·26	55·11
15	30·08	3·80	66·12	9·41	37·10	53·49
16	30·91	3·76	65·33	9·82	37·16	53·02
17	31·39	3·75	64·86	8·60	38·87	52·60
18	32·14	3·77	64·09	9·41	38·11	52·48
19	32·36	3·85	63·79	10·89	36·10	53·01
20	30·79	3·87	65·34	19·16	24·78	56·06
21	32·48	3·04	64·48	11·68	37·60	50·72
22	32·97	2·91	64.12	11·30	39·60	49·10
23	33·09	2·82	64·09	12·27	44·02	45·71
24	33·56	2·81	63·63	17·20	31·44	51·36
25	34·03	2·96	63·01	36·52	10·58	52·90
26	33·89	2·99	63·12	44·39	0·91	54·70
27	34·80	1·45	63·75	43·24	0·65	56·11
28	35·86	...	64·14	...	...	...

TABLE 8.

$100mH_2O \cdot xMgCl_2 \cdot (100-x)MgSO_4$

No.	Solution		Residue		
	x	m	x	m	Solid phase
1	0·00	18·31	...	...	$MgSO_4.7H_2O$
2	7·75	18·61	1·60	9·59	„
3	25·51	18·97	—	—	„
4	44·46	18·80	9·72	9·82	„
5	48·72	18·39	9·60	9·37	„
6	62·48	17·60	14·48	9·47	„
7	62·80	16·48	13·48	8·96	„
8	66·95	15·99	13·94	8·96	„
9	84 57	13·43	14·47	8·12	„
10	86·81	12·08	19·94	7·72	$MgSO_4.7H_2O$; $MgSO_4.6H_2O$
11	87·20	11·96	24·59	7·72	$MgSO_4.6H_2O$
12	89·16	11·43	8·50	6·81	„
13	89·13	11·21	30·94	7·88	„
14	89·80	11·04	28·21	7·69	„
15	90·92	10·51	24·32	7·27	„
16	91·22	10·14	25·08	7·12	„
17	91·38	9 93	21·89	7·04	„
18	91·54	9·60	23·82	6·99	„
19	91·40	9·48	27·65	7·08	„
20	90·97	10·15	49·48	7·62	$MgHO_4.5H_2O$
21	93·11	9·72	28·24	6·45	„
22	93·49	9·56	25·34	6·17	„
23	93·70	9·55	22·81	5·34	$MgSO_4.4H_2O$
24	93·80	9·36	40·94	6·43	„
25	93·58	9·11	81·39	6 20	$MgSO_4.4H_2O$; $MgCl_2.6H_2O$
26	93·46	9·16	98·39	6·38	$MgCl_2.6H_2O$
27	96·82	9·33	98·84	6·75	„
28	100·00	9·41	...	...	„

Fg. 4.

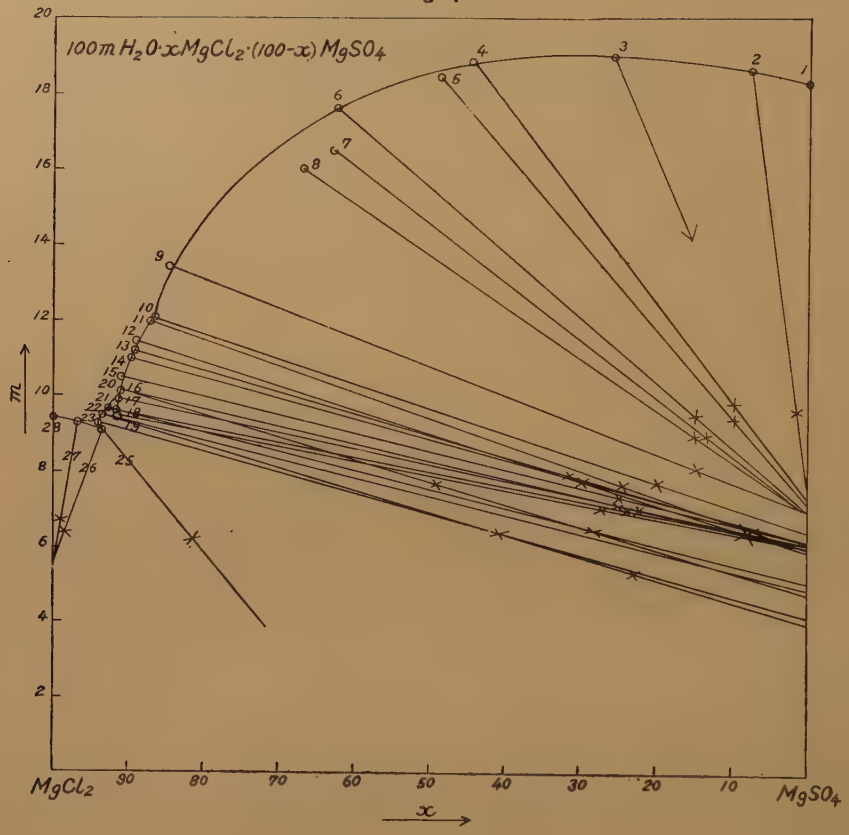
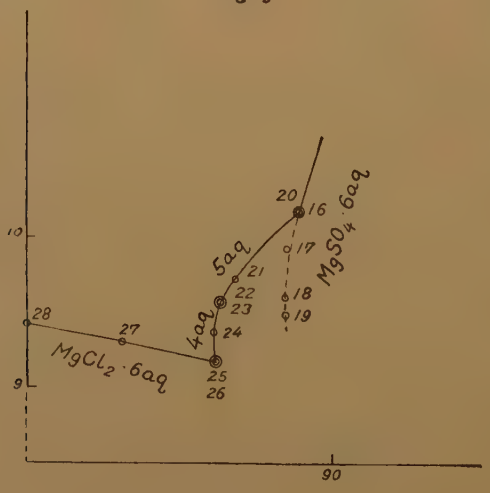

100m H2O·xMgCl2·(100-x) MgSO4
m
x
MgCl2
MgSO4

Fig. 5.


MgCl2·6aq
4aq
5aq
MgSO4·6aq

It may be clearly seen from Fig. 4 that the solid phases of this system are $MgSO_4.7H_2O$, $MgSO_4.6H_2O$, $MgSO_4.5H_2O$, $MgSO_4.4H_2O$, and $MgCl_2.6H_2O$. Thus van't Hoff's observation was confirmed qualitatively, but quantitatively there are some differences.

That part of the diagram where the opinions of previous investigators are not in agreement, was studied with special care in the present work. Fig. 5 is drawn to expose this part on a greater scale. It may be seen from Fig. 5 that the hexahydrate has the transition point to the pentahydrate at the point 16, but the curve for the hexahydrate might be further continued as represented by the points 17, 18, and 19. From the relative position of the curves for the hexa and penta hydrates, it is beyond doubt that the three latter points represent metastable equilibria.

The compositions of solutions, represented by points 16 and 20 in Fig. 5, and having the hexa- and penta-hydrates as residue respectively, are almost the same, and it may be permitted to take the average values of them as the composition of a solution saturated with these two hydrates. They are

$$x = 91{\cdot}10, \qquad m = 10{\cdot}15.$$

In a similar way, the composition of the solution saturated with the penta- and tetra-hydrates of magnesium sulphate, is determined at the points 22 and 23 as follows:

$$x = 93{\cdot}60, \qquad m = 9{\cdot}56.$$

Thus the existence of the penta- and tetra-hydrates of magnesium sulphate was confirmed. Though Löwenherz and also Blasdale believe that they had obtained a solution saturated with the hexahydrates of magnesium sulphate and of magnesium chloride, it is evident from the present investigation that the hydrate of magnesium sulphate which coexists with the hexahydrate of magnesium chloride in stable equilibrium is the tetra- and not the hexahydrate.

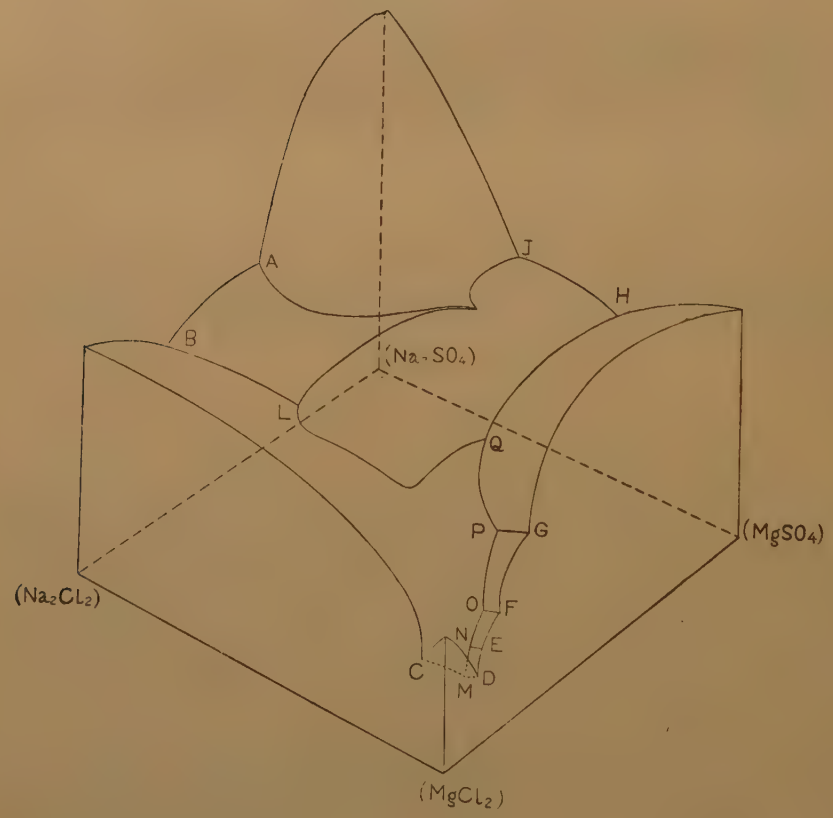
The following observation may be added as an evidence of the existence of the lower hydrates of magnesium sulphate. The crystals of the hexahydrate in equilibrium flasks were somewhat translucent, but as soon as they changed into the lower hydrates, they became opaque.

3. The reciprocal salt pairs of sodium chloride and magnesium sulphate, and sodium sulphate and magnesium chloride at 25°.C.

There are two methods for the graphical representation of the equilibrium of reciprocal salt pairs, one referring to octahedral coordinates first used by R. Löwenherz[1] and the other referring to the quadratic prism proposed by E. Jänecke.[2] Since the second mode of representation is simpler and more convenient, it is adopted here to reproduce the results of the work.

Fig. 6 represents a model of the system, Fig. 7 is its horizontal projection, and in Fig. 8, a portion of it is reproduced in a larger

Fig. 6.



1 Zs. physik. Chem., **13**, 459 (1894).
2 Zs. anorg. Chem., **15**, 132 (1906).

scale. The vertices of the square represents the four single salts respectively as indicated in the figure. The sides represent the equilibria of the systems of two salts, with a common ion, and water, and they are nothing but the projections of the rectangle diagram of those ternary systems on the horizontal side, which have been already described.

Fig. 7.

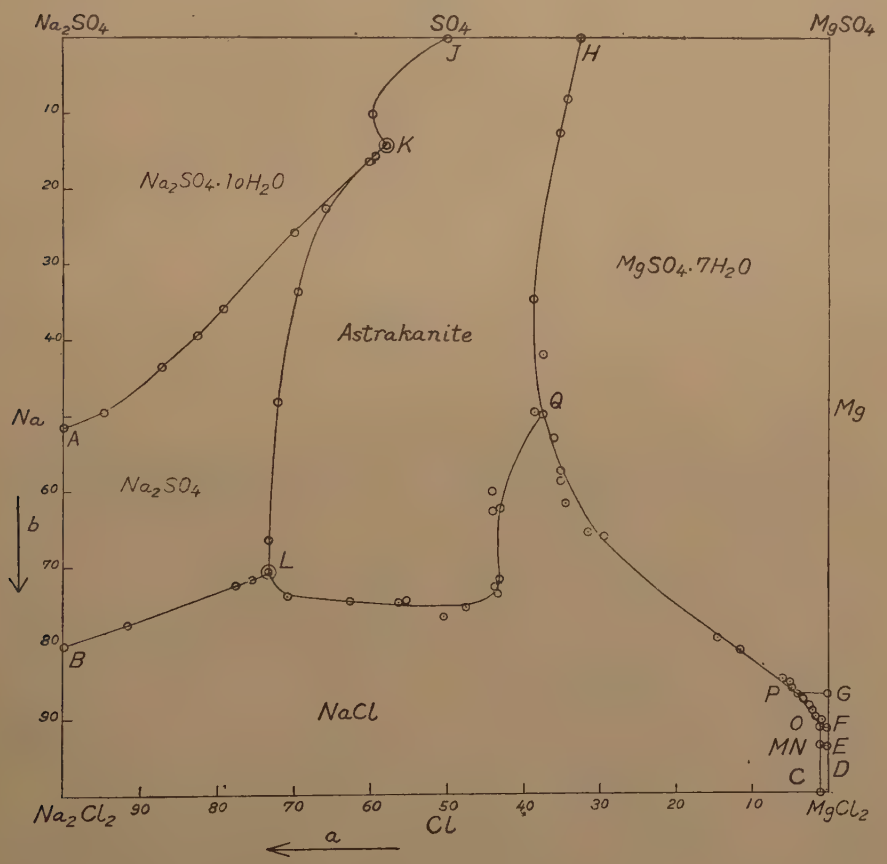
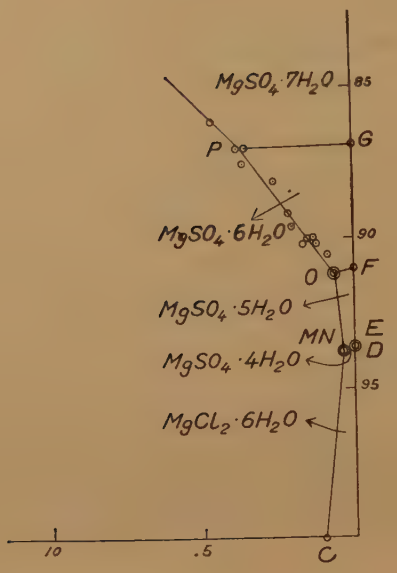


Fig. 8



Now, the experimental method, by which the data necessary for the construction of the model and Fig. 7 were sought, and the results thus obtained will be described.

The experiments were carried out in the following way: Into a solution saturated with two salts having the common ion, another salt was added in different proportions, and it was so arranged that, when equilibrium was attained, two or three salts remained as residue. Then the solution was analyzed.

The composition of the solution was represented by the formula:

$$100mH_2O.aNa_2.(100\text{-}a)Mg.bCl_2.(100-b)SO_4$$

and by the values of a and b, the position of the points representing the solution in the diagram was determined. Fig 7 was obtained as the results of such determinations and some details about the diagram will be given in the following pages.

The curve: AK.

The solutions, represented by the points on this curve, have always $Na_2SO_4.10H_2O$ and Na_2SO_4 as the residue, and they change

from A to K along this curve when the concentration of magnesium salts increases. When K is reached, a new solid phase, astrakanite, comes into existence. The data for some points on the curve are given in the following table.

TABLE 9.

No.	a	b	m
A	100·00	51·31	18·03
1	94·55	49·40	17·07
2	87·33	43·49	16·33
3	82·84	39·10	16·21
4	79·03	35·94	15·89
5	69·89	25·77	14·74
7	59·77	15 71	13·94
7	59·63	15·58	13·81
K	57·92	14·05	13·71

The curve : JK.

The solutions, represented by the points on the curve, have always astrakanite and $Na_2SO_4.10H_2O$ as the residue and when K is reached, a new solid phase, Na_2SO_4, separates out.

TABLE 10.

No.	a	b	m
J	49·86	0·00	13·97
	60·00	9·96	13·68
K	57·98	13·70	13·64

The values for the point K in table 9 is in good agreement with those in table 10, and the means are taken as the values for K as follows :

K : a = 57·95, b = 13·88, m = 13·66.

The corresponding values found by Blasdale are

a = 80·47, b = 40·42, m = 16·92.

There is a great discrepancy between the two sets of values. In the author's experiments for the points on the curve AK, the residue in every equilibrium flask was examined for magnesium and first, when the composition of solution reached the point K, a noticeable amount of magnesium was found in the residue. Moreover the fact that the data for K found along the curve AK is in fair agreement with those found along the curve JK makes it very probable that the values now found are the true ones for the solution having Na_2SO_4, $Na_2SO_4.10H_2O$, and astrakanite as the residue.

The curve: BL.

The solutions, represented by the points on this curve, have always Na_2SO_4 and NaCl as the residue and when L is reached, a new solid phase, astrakanite, comes to appearance.

TABLE 11.

No.	a	b	m
B	100·00	80·40	15 96
1	91·70	77·63	15·67
2	77·57	72 40	15·10
3	75·55	71·55	15·10
L	73·35	70·70	15·06

The curve: KL.

The solutions, represented by the points on this curve, have always Na_2SO_4 and astrakanite as the residue, and when the curve reaches K or L, a new residue, $Na_2SO_4.10H_2O$ or NaCl comes to existence in addition respectively.

TABLE 12.

No.	a	b	m
K	57·95	13·88	13·66
1	66·15	22·45	14·67
2	69·32	33·51	15·02
3	72·10	48·09	15·64
4	73·65	66·52	15·47
L	73·40	70·61	15·06

The data for L in Tables 11 and 12 are in fair agreement with each other, so the respective mean values of them are taken as the correct ones, namely:

L: a=73·38, b=70·66, m=15·06.

The corresponding data found in the literature are as follows:

a=71·38, b=72·71, m=15·19 (Blasdale)
a=74·8, b=70·3, m=15·3 (van't Hoff)

The curve: QL.

The solutions, represented by the points on this curve, have always NaCl and astrakanite as the residue; and when the point Q is reached, a new solid phase, $MgSO_4.7H_2O$, comes into existence.

TABLE 13.

No.	a	b	m
L	73·38	70·66	15·06
1	70·98	73·84	15·40
2	62·86	74·62	15·34
3	56·18	74·70	15·14
4	55·29	74·53	15·12
5	50·75	76·29	15·16
6	47·62	75·10	15·11
7	43·32	73·73	15·38
8	43·78	72·72	15·32
9	43·26	72·05	15·14
10	43·77	63·74	13·92
11	43·46	62·67	13·98
12	44·39	60·01	13·95
Q	38·52	49·55	13·94

The curve: HQ.

The solutions, represented by the points on this curve, have always $MgSO_4.7H_2O$ and astrakanite as the residue; and when the point Q is reached, a new solid salt, NaCl separates out.

TABLE 14.

No.	a	b	m
H	32·72	0·00	13·69
1	34·44	8·02	13·97
2	35·75	12·28	14·00
3	38·64	34·67	14·15
4	37·66	41·88	14·04
Q	37·42	49·87	13·98

As the data for Q in Tables 13 and 14 are practically the same, the respective mean values of them are taken as the correct ones for Q, namely:

Q: a=37·97, b=49·71, m=13·96.

The corresponding data found in the literature are as follows:

a=21·00, b=74·94, m=13·93 (Blasdale)
a=38·8, b=49·3, m=14·9 (van't Hoff)

The author's data are very near to van't Hoff's and greatly different from Blasdale's. When the curve was followed from the point H by increasing the amount of chloride radical gradually, very fine crystals of astrakanite, difficult to settle, were always observed in the interval between H and Q, but as soon as the solution passed over Q, such a phenomenon could be recognized no more. Moreover, a noticeable amount of chloride radical was first found in the residue at Q. Thus, it will not be unreasonable to take the data, above obtained, as the correct composition of the solution saturated with those three salts.

The point: M.

The point, representing the solution saturated with $MgCl_2.6H_2O$, NaCl, and $MgSO_4.4H_2O$ was determined as follows:

	a	b	m
	0·29	93·79	9·29
	0·18	93·75	9·25
M:	0·24	93·77	9·27

van't Hoff's data, corresponding to this, are

$$a=0{\cdot}9, \quad b=95{,}3, \quad m=9{\cdot}3.$$

The space, enclosed by C, M, and D, is the field of $MgCl_2.6H_2O$, and the point D corresponds to a solution saturated with $MgCl_2.6H_4O$ and $MgSO_4.4H_2O$.

The point: N.

In the ternary system, magnesium chloride, magnesium sulphate, and water, the solution saturated with $MgSO_4.4H_2O$ and $MgCl_2.6H_2O$ and that saturated with $MgSO_4.4H_2O$ and $MgSO_4.5H_2O$ contain the two salts almost in the same ratio, as seen in Fig. 5. So in Figs. 7 and 8, the points D and E representing the respective solutions can not be distinguished.

A great deal of trouble was taken to obtain such a solution saturated with NaCl, $MgSO_4.5H_2O$, and $MgSO_4.4H_2O$, which is represented by an assumed point N, but it was in vain, as the solution represented by the point O which is saturated with $MgSO_4.5H_2O$, $MgSO_4.6H_2O$, and NaCl always resulted. Van't Hoff assigned the following composition to that point N:

$$a=1{\cdot}1, \quad b=91{\cdot}6, \quad m=10{\cdot}5.$$

But in the present investigation, taking the data for the curves DM and OP, and the point D in consideration, it may be estimated as

N: $a=0{\cdot}25, \quad b=93{\cdot}7, \quad m=9{\cdot}5$

The point: O.

The point representing the solution saturated with $MgSO_4.5H_2O$, NaCl, and $MgSO_4.6H_2O$ was determined as follows:

	a	b	m
	0·75	91·21	9·91
	0·64	91·14	10.08
	0·64	91·01	10·11
O:	0·68	91·12	10·03

van't Hoff's data for it are as follows:

$$a=2{\cdot}1, \quad b=99{\cdot}4, \quad m=10{\cdot}6$$

The curve: OP.

The solutions, represented by the points on this curve, have always $MgSO_4.6H_2O$ and NaCl as the residue; and when the point P is reached, a new residue, $MgSO_4.7H_2O$, comes also into existence.

TABLE 15.

No.	a	b	m
O	0·68	91·12	10·03
1	0·89	90·49	10·64
2	1·70	90·17	10·81
3	1·37	90·00	10·75
4	1·34	90·15	10·76
5	1·57	90·00	10·95
6	2·10	89·70	10·93
7	2·04	89·31	11·17
8	2·61	88·11	11·57
9	3·55	87·49	11·77
{	3·92	87·08	11·90
{	3·62	87·00	11·94
P	3·77	87·04	11·92

But van't Hoff's data for the solution corresponding to the point P are as follows:

$$a = 13{\cdot}4, \qquad b = 80{\cdot}8, \qquad m = 12{\cdot}7.$$

As may be seen, the difference between the two observations is very considerable.

The curve: PQ.

The solutions, represented by the points on this curve, have always NaCl and $MgSO_4.7H_2O$ as the residue.

TABLE 16.

No.	a	b	m
P	3·77	87·04	11·92
1	4·63	86·21	12·18
2	4·98	85·62	12·41
3	6·13	85·04	12·62
4	11·63	80·93	13·41
5	14·26	79·35	13·58
6	29·58	66·02	13·94
7	31·83	65·21	13·98
8	34·61	61·88	13·81
9	35·15	58·40	13·93
10	35·14	57·20	14·00
11	36·10	53·11	14·04
Q	37·97	49·71	13·96

SUMMARY.

There exist nine kinds of solid phases in the system of equilibrium of the reciprocal salt pairs of sodium chloride and magnesium sulphate, and sodium sulphate and magnesium chloride at 25°C., namely, $Na_2SO_4.10H_2O$, Na_2SO_4, NaCl, astrakanite, $MgSO_4.7H_2O$, $MgSO_4.6H_2O$, $MgSO_4.5H_2O$, $MgSO_4.4H_2O$, and $MgCl_2.6H_2O$.

The special points representing the saturated solutions of a single, two, or three salts are summarized in the following table.

TABLE 17.

	Solid phase	a	b	m
	$NaCl$	100	100	18·02
	$MgSO_4.7H_2O$	0	0	18·31
	$Na_2SO_4.10H_2O$	100	0	28·51
	$MgCl_2.6H_2O$	0	100	9·41
B	$NaCl$; Na_2SO_4	100	80·40	15 96
A	Na_2SO_4; $Na_2SO_4.10H_2O$	100	51·31	18·03
C	$NaCl$; $MgCl_2.6H_2O$	1·08	100	9·32
H	$MgSO_4.7H_2O$; Astrakanite	32·72	0	13·69
J	Astrakanite; $Na_2SO_4.10H_2O$	50·14	0	13·97
G	$MgSO_4.7H_2O$; $MgSO_4.6H_2O$	0	86·81	12·08
F	$MgSO_4.6H_2O$; $MgSO_4.5H_2O$	0	91·10	10·15
E	$MgSO_4.5H_2O$; $MgSO_4.4H_2O$	0	93·60	9·56
D	$MgSO_4.4H_2O$; $MgCl_2.6H_2O$	0	93·58	9·11
K	$Na_2SO_4.10H_2O$; Na_2SO_4; Astrakanite	57·95	13·88	13·66
L	Na_2SO_4; $NaCl$; Astrakanite	73·38	70·66	15·06
Q	$NaCl$; Astrakanite; $MgSO_4.7H_2O$	37·97	49·71	13·96
P	$NaCl$; $MgSO_4.7H_2O$; $MgSO_4.6H_2O$	3·77	87·04	11·92
O	$NaCl$; $MgSO_4.6H_2O$; $MgSO_4.5H_2O$	0·68	91·12	10·03
N	$NaCl$; $MgSO_4.5H_2O$; $MgSO_4.4H_2O$	0·25	93·7	9·5
M	$NaCl$; $MgSO_4.4H_2O$; $MgCl_2.6H_2O$	0·24	93·77	9·27

In conclusion the author wishes to express his sincere thanks to Prof. Y. Osaka for his valuable suggestions and kind instructions.

On a Mica X-Ray Spectrometer.

By

Usaburo Yoshida.

(Received August 26, 1920.)

A convenient x-ray spectrometer of bent mica was first devised by de Bloglie and Lindemann[1], and by Rohmann[2] simultaneously. The former workers[3] obtained an x-ray spectrum of the L series of platinum up to its sixth order by this instrument, and they showed that the grating constant d of mica was about 10×10^{-8}cm. Next, a quite different result was obtained by Gorton[4]. From the measurement on the spectrum of tungsten he concluded that the mica had four reflecting sets of planes parallel to the cleavage face, and that the four grating constants corresponding respectively to these four sets were in no simple rational relation to each other. Gorton's conclusion is inconceivable with our actual knowledge, and it was already pointed out by Siegbahn[5] that Gorton's result was based on a false assumption.

The measurement of the wave lengths of x-rays by previous experimenters with the bent mica x-ray spectrometer was not so accurate as with the other spectrometers. And as it seemed to the writer not to be valueless to test how accurately the wave length was determinable with this spectrometer, the author has undertaken essentially the same experiment as that of Gorton.

The spectrometer used is represented diagramatically in Fig. 1. B represents a lead box, and S the slit the width of which is

1 De Broglie and Lindemann, C. R., **158**, 944, (1914).
2 Rohmann, Phys. Z.S., **15**, 510, (1914).
3 De Broglie and Lindemann, j. de Phys., **4**, 265, (1914).
4 Gorton, Phys. R., **7**, 335, (1916).
5 Siegbahn, Phys. R., **8**, 320, (1916).

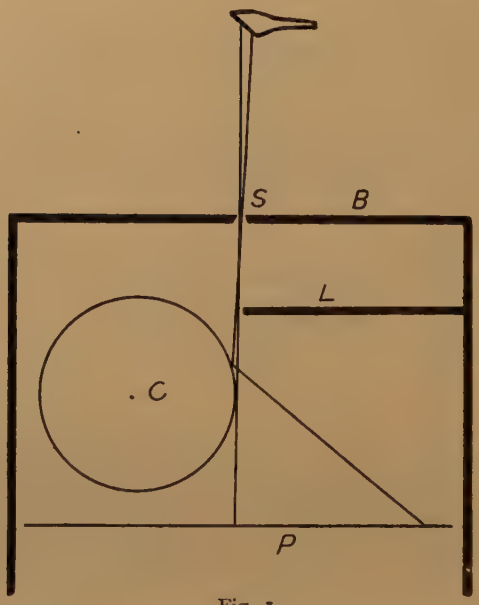


Fig. 1.

0.3 mm. C is a wooden cylinder of radius 36.39 mm., and on its surface a sheet of mica of a thickness of 0.07 mm. is just fastened. Consequently the radius of the cylindrical mica is 36.46 mm. This cylinder of mica is placed in such a position that the perpendicular from the slit S to the plane of the photographic plate P is exactly in the position of a tangent to the cylinder. A lead screen L is placed in a proper position to prevent the one half of photographic plate from being attacked by the direct rays from the x-ray tube. The mica to be used as the reflector was carefully examined, and a pretty good one free from deformation and other irregularities was selected.

A Coolidge x-ray tube having a tungsten anticathode was employed in the present experiment. The time of exposure was from one to three hours, using currents of the order of 4 milliamperes and the potential differences of from 40 to 70 kilovolts.

An example of the photographs obtained is reproduced in Fig. 3. The spectrum lines of the L series of tungsten are visible on the photograph up to the fifth order, those in the third and fifth order being superior in intensity to the others. Here it is to be noted that

some faint lines which were visible on the original plate are absent in the reproduction.

The relation between the distance of a spectrum line from the zero position on the photographic plate and the glancing angle of the ray on the cleavage face of the mica crystal may be calculated simply in the following way:

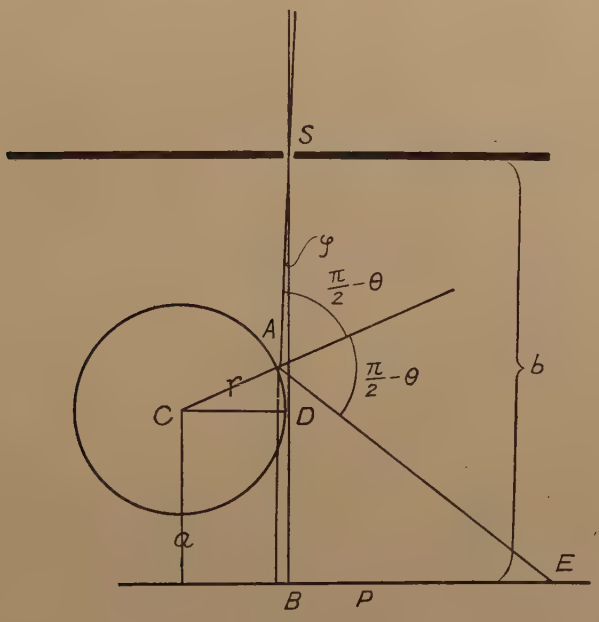


Fig. 2.

In Fig. 2, S is the slit through which the x-rays advance toward the photographic plate P. The path of the ray which is tangential to the cylindrical mica and perpendicular to the photographic plate is denoted by the straight line SB, and that of the ray which impinges on the mica at A and is reflected toward AE is represented by SA. Let φ be the angle ASB, and θ the glancing angle of the ray SA to the cleavage face of the mica at A, r the radius of the cylindrical mica, b the distance between the slit and the photographic plate P, and a the distance between the center of the cylinder C and the photographic plate P. Then the relation between φ and θ is given by the formula

$$\tan\varphi = \frac{r\{1-\cos(\theta-\varphi)\}}{b-a-r\sin(\theta-\varphi)}.$$

The values of r, a and b were 36.46 mm., 51.9 mm. and 156.7 mm. respectively in the present case. Making use of these values, the numerical value of φ corresponding to a given value of θ may be calculated by the method of successive approximation. Next let x be the distance between B and E, then the value of x corresponding to a given value of θ may be calculated by the formula

$$x = \{a+r\sin(\theta-\varphi)\}\tan(2\theta-\varphi)-r\{1-\cos(\theta-\varphi)\}.$$

Thus the relation between the values of x and $\sin\theta$ being expressed by a curve, the value of $\sin\theta$ corresponding to a given value of x may be obtained immediately.

Here it must be noted that the zero position B on the photographic plate in Fig. 2, where the ray which was tangential to the cylindrical mica attacked the plate, was well defined in the original plate, as the shadow of the mica cast by the x ray, though it is not visible in the reproduction. This was very favorable and convenient for accurate determination of the zero position.

TABLE I.

d in A.U.

order		γ_3	γ_2	γ_1	β_2	β_3	β_1		β_4	α_1	α_2	mean value of d
1	$\sin\theta$			0.0553	0.0626		0.0644			0.0743		
	d											
2	$\sin\theta$			0.1107	0.1254	0.1272	0.1291		0.1309	0.1486		
	d			9·897	9.903	9.906	9.909		9.921	9.917		9.909
3	$\sin\theta$			0.1658	0.1881	0.1906	0.1937	0.1947	0.1965	0.2231	0.2246	
	d			9.911	9·903	9.916	9.906		9.915	9.908	9.914	9.910
4	$\sin\theta$			0.2213	0.2506		0.2581			0.2976		
	d				9.911		9.913			9.905		9.909
5	$\sin\theta$	0.2669	0.2684	0.2764	0.3132	0.3176	0.3224		0.3272	0.3718		
	d			9.910	9.912	9.921	9.919		9.921	9.907		9.915
mean value of d												9.911

TABLE II.

Wave lengths in A.U.

order	γ_3	γ_2	γ_1	β_2	β_3	β_1		β_4	α_1	α_2
1			1.096	1.241		1.277			1.473	
2			1.097_2	1.242_8	1.260_0	1.279_5		1.297_4	1.472_8	
3			1.095_2	1.242_8	1.259_5	1.279_9	1.286_3	1.298_4	1.474_2	1.484_0
4			1.096_5	1.241_9		1.279_0			1.474_8	
5	1.058	1.064	1.095_8	1.241_7	1.259_1	1.278_2		1.297_2	1.474_0	1.485_0
Mean	1.058	1.064	1.096_2	1.242_3	1.259_5	1.279_2	1.286_3	1.297_7	1.474_0	1.484_5
Siegbahn	1.05965	1.06584	1.09553	1.24191	1.26000	1.27917	1.2871	1.29874	1.47348	1.48452
Dershem	1.059	1.065	1.095	1.242	1.259	1.278	1.287	1.298	1.472	1.483

The results of the measurement are tabulated in the tables I and II. The grating constant d for the mica was calculated by the relation $2\,d \sin\theta = n\lambda$, by assigning proper values to n and λ corresponding to each observed value of $\sin\theta$. For the wave length λ, the values recently given by Siegbahn[1] for the L series of tungsten was employed. As may be seen from Table I, the value of the grating constant d determined from every line is in fair agreement with each other. The mean value of d calculated from those of the lines in all the orders from the second up to the fifth is 9.911 A.U., which is smaller by one per cent. than that given by de Broglie and Lindemann.

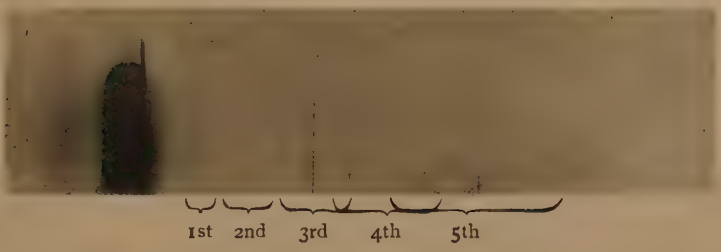
Next, taking the grating constant d of the mica as 9.911 A.U., the wave lengths of the lines observed were calculated reversely, and are given in Table II. The observed values are in fair agreement with those given by Siegbahn and Dershem,[2] and they differ only by small quantities less than 0.2 per cent from those given by the other observers.

In conclusion, the writer wishes to express his sincere thanks to Prof. T. Mizuno for the interest he has taken in the research.

1 Siegbahn, Phil. Mag., **38**, 639, (1919).

2 Dershem, Phys. R., **11**, 471, (1918).

Fig. 3.



On the Colour of Coloured Fluorites

By

Tokutaro Sakao and Mitsuie Hirose

(Received September 17, 1920)

The cause of the colours of Blue John and other varieties of fluorite has long been a matter of doubt and controversy. Messrs. Blount and Sequeira carried out an interesting investigation on the problem, and the result was briefly described in the Transactions of the Chemical Society.[1]

According to their conclusion there is no substantial difference between a white fluorite and blue, green and amethystine varieties, except the presence of a small amount of organic matter, and the colours are ascribed to this organic matter. But the state of dispersion of the latter is not discussed.

Now it is already ascertained that the blue colour of certain varieties of rock salt is due to a colloidal dispersion of sodium in sodium chloride, and that the blue colours of sodalite and ultramarine are almost certainly due to a similar cause. As was suggested in *Nature*,[2] though the colour of the fluorites is ascribed to the presence of some organic matter, yet the problem is not completely solved. The present writers, under the suggestion of Prof. M. Kimura, attempted an experiment to examine by means of an ultra-microscope the state of the suspected organic matter in the crystal, and a short account of the result obtained will be given below.

In the present experiment the following specimens were selected and examined.

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1 Vol. 115, 705 (1919).

2 *Nature* Sept. 13, 1919.

(1) a piece of a transparent crystal, one half of which was coloured amethystine, while the remaining part exhibits a green colour,

(2) a piece of a green fluorite having a transparent stria,

(3) a piece of perfectly transparent fluorite,

(4) two pieces of green fluorite, one of which is more deeply coloured than the other,

(5) a colourless crystal obtained by baking a piece of a green variety.

Small pieces of the crystal mentioned above were selected from several pieces of the crystal; and they were cut into parallel plates having a thickness about 1 mm., and then the surfaces were polished with emery and then rouge to secure an optical surface. The plates prepared were examined with an ultra-microscope having a cardioid condenser, illuminated by the light from a 20-ampere carbon arc.

In all the coloured specimens mentioned above a uniform distribution of an immense number of particles as is usually seen in the case of coloured glasses and of colloidal solutions could not be detected at all, the only thing observed being a very few bright particles. These particles were distributed very irregularly and their number varied from plane to plane within the crystal, the total number seen in a field of view being not greater than about ten.

In a transparent portion of the crystal such particles were also observed, and their number and mode of distribution did not present a sensible difference even in crossing at the boundaries of a transparent stria in the green fluorite. Moreover, in certain specimens it was ascrtained that a weakly coloured crystal contains a larger number of the bright particles than a highly coloured one.

These facts seem to indicate that the particles under consideration have no relation with the cause of the colour of the fluorite. As to the nature of these particles no definite conclusion can be drawn from the present experiment, but we may considered that the particles might be minute holes or some impurities contained within the crystal.

If the particles were totally taken out of consideration the coloured fluorite is optically clear. This means that if the organic matter found by Blount and Sequeira be in a state of colloidal suspension, it should have the same index of refraction as that of the fluorite, or that the colloidal particles should be too fine to be detected in the present experiment. Otherwise, the organic matter would be scattered into the molecular state in the crystal.

The Absorption of Light by Sulphur at various Temperatures

By

Mitsuharu Fukuda

(Received September 17, 1920)

It is well known that sulphur changes its colour when heated. This is due to a shift of the absorption band. Generally, the absorption band of a substance moves toward the less refrangible side as its temperature rises. The writer made an experiment to study how the absorption band of sulphur shifts with the variation of the temperature, and the result obtained is given below.

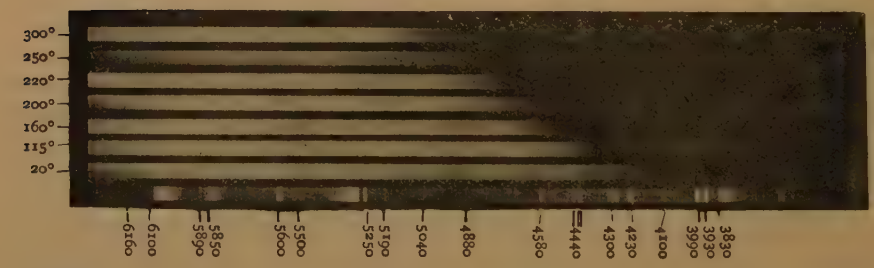
A thin layer of sulphur whose absorption was to be studied was prepared in the following way: a small quantity of the substance was put between two glass plates, and this was slowly heated by a Bunsen-burner until the whole was uniformly melted.

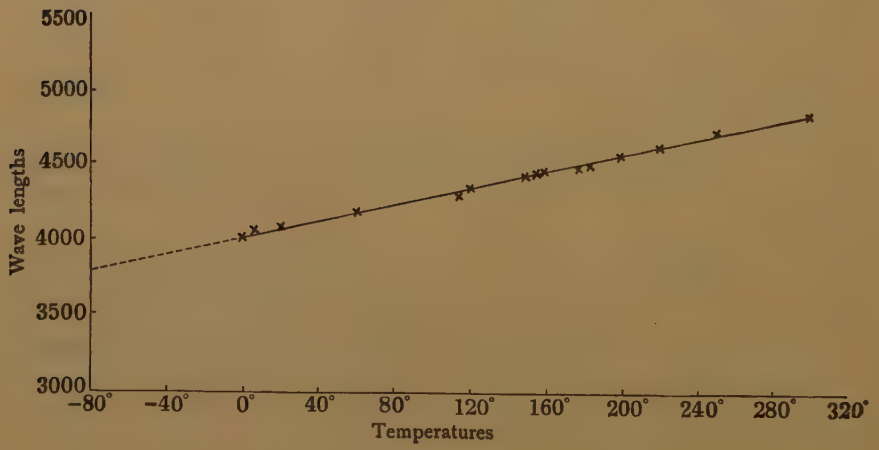
One junction of a thermo-couple consisting of platinum and tungsten was then inserted into the melted sulphur, and the whole was uniformly heated in an air-bath, the temperature of the other junction being kept constant by means of running water. The above thermo-couple consisted of fine wires of platinum (0·02 mm. dia.) and tungsten (0·035 mm. dia.), they being joined together in a flame of a carbon arc. The couple thus made was previously calibrated up to 300°C. in vacuum oil, the temperature of which being determined by a mercury thermometer.

Next, the absorption spectra of the sulphur at various temperatures were examined with a spectrograph having a replica grating. As the source of light, a carbon arc fed with a salt of calcium was used, and wave lengths of an edge of the absorption bands at various

temperatures were determined from the reference lines of calcium. The wave lengths of the edge of the absorption bands determined from these photographic plates did not differ more than 3 $\mu\mu$. The wave lengths of one edge of the absorption band at various temperatures are given in the following table, and the relation between them is seen from the accompanying figure.

Temperature of the Sulphur	Absorption
0°C.	From ultra-violet to λ 0·408 μ
20° „	„ λ 0·410 „
60° „	„ λ 0·420 „
115° „	„ λ 0·430 „
120° „	„ λ 0·435 „
160° „	„ λ 0·446 „
180° „	„ λ 0·450 „
200° „	„ λ 0·458 „
210° „	„ λ 0·460 „
250° „	„ λ 0·473 „
300° „	From ultra-violet to λ 0·488 μ (Thickness of sulphur: 0·3 mm.)





Thus, the less refrangible edge of the absorption band of sulphur proceeds toward the red as its temperature was raised, and within the range of the experiment, the rise of the temperature by 10°C. produces a shift of about 2 $\mu\mu$.

According to the investigation of Kellas,[1] the molecular complexity of the liquid sulphur between 115°C. and 160°C. was represented by S_6, while polymerization from S_6 to S_{18} occurs at a temperature of about 160°C., the latter remaining stable up to the temperature of the boiling point of the sulphur. Now, if the molecular complexties S_6 and S_{18} would absorb different parts of the spectrum, the absorption band of the sulphur should change suddenly in the neighborhood of 160°C., so that an abrupt bending or discontinuity might be expected in the above line. In the experiment described above, many photographs were taken especially in the neighbourhood of this temperature. No trace of any bending or discontinuity was, however, observed, the edge of the absorption band extending gradually toward the red with the rise of temperature.

Now, if the straight line in the above figure is produced toward the negative side of the temperature axis, it will pass the point (λ=0·390 μ, T=−50°C.). Since λ0·397 μ is the violet end of the visible spectrum the above indicates that the sulphur will transmit all the visible part of the spectrum when cooled down below −50C°. This confirms the observation of the previous investigators.

Next, the absorption of light by sulphur in a plastic state was studied.

Temp. of Sulphur		Edge of Absorption Band		
before cooling	after cooling	before cooling	after cooling	untreated one corresp. to temps. given in the second colum
300°C.	100°C.	0.488 μ	0.453 μ	0.418 μ
„	50°C.		0.441 „	0.418 „
„	20°C.		0.435 „	0.410 „
„	10°C.		—	9.405 „
200°C.	100°C.	0.458 „	8.440 „	0.428 „
„	5c°C.		0.434 „	0.418 „
„	20°C.		—	0.410 „
„	10°C.		0.430 „	0.405 „

1 J. Chem. Soc. 113. pp 903–922. 1918.

The sulphur was first heated to a high temperature and this was then suddenly put into water at various temperatures. The plastic sulphur thus prepared was squeezed between a pair of glass plates, and this was examined in the way described above. The result is given in the above table.

From this, we see that the absorption of light by the plastic sulphur is not simply determined by its present temperature, but it also depends upon the initial temperature to which the sulphur was previously heated. The higher the initial temperature, the longer is the wave length of the edge of the absorption band.

Now, sulphur has two modifications S_6 and S_{18}, and if the sulphur at 300°C. was gradually cooled down to 100°C. for example, S_{18} would completely transform into S_6, but if it was rapidly cooled, this is not the case, because its absorption spectrum corresponds to that of a higher temperature of about 180°C. Thus, the plastic sulphur will consist of S_6 and S_{18} mixed in a complex way.

In conclusion, the writer wishes to express his thanks to Prof. M. Kimura for his kind guidance.

On the negatively charged Particles in the Positive Ray Tube.

By

Matakichi Ishino and Bunsaku Arakatsu.

(Received September 21, 1920).

The negatively charged particles in the positive ray tube has been investigated by J. J. Thomson. The results he obtained may be summarized as follows:

(i). The atoms of hydrogen, carbon, chlorine, and sulphur occur with a negative charge, but those of helium, nitrogen, neon, krypton, xenon, and vapour of mercury do never so appear.

(ii). The molecule of a compound with a negative charge does not occur at all; but a few kinds of molecules of certain elements, namely, O_2, C_2, O_3, H_3, with a negative charge are fonnd in some exceptional cases.

(iii). The radicles of OH and CN with a negative charge are observed.

The aim of the present paper is to furnish some further knowledge on the negatively charged particles observed in the positive ray analysis.

The method of photographing the positive rays is quite the same as that described in a former paper[1] by one of the present authors. The experiments were carried out with the gases of chlorine, hydrogen sulphide, sulphur dioxide, and the vapours of carbon bisulphide and nitric acid, introduced into the discharge bulb. The results of the examination of the lines on the photographic plates are given below.

1 M. Ishino, "On the Evidence of the Existence of Isotopes of Chlorine," in this number of the Memoir.

(1). Negatively charged atoms.

In agreement with J. J. Thomson's results, the carriers of the negative charge were commonly found in the atomic type. The atoms of hydrogen, carbon, and oxygen were found in almost every case. The intensity of the parabola due to O^- was sometimes stronger than that due to O^+. When chlorine was present in the discharge bulb, the two isotopes, Cl_I and Cl_{II}, with negative charge were conspicuous.[1] When CS_2 or SO_2 was introduced into the tube, negatively charged sulphur atoms were found.

(2). Negatively charged molecules of elements.

In the case of CS_2 a very faint line due to C_2^- was observed. (Fig. 1 in Plate I.) Negatively charged molecules of oxygen are very seldom noticed. These facts are in accordance with Thomson's results.

(3). Negatively charged molecules of Compounds or Radicles.

Contrary to Thomson's result, we have often met with some cases in which the molecule of a compound has been found with a negative charge. When H_2O_2 gas was present in the tube, the negatively charged molecules of H_2O made appearance. This line was ascribed at first to OH^-, but repeated measurements of the value of $\frac{e}{m}$ show the line to be H_2O^-. (See Fig. 2 in Plate I.). In the case where CS_2 gas was present, particles of SO^- and SO_2^- were observed (See Fig. 1 in Plate I.). With the vapour of nitric acid the line of NO^- has appeared. (See Fig. 3 in Plate I). In some cases a trace of CN^- could be observed. Now it is here highly desirable to notice that the molecules and radicles SO, SO_2, NO, are all chemically very active, and at the same time strongly eleetro-negative.

All the main beads of the negative parabolas due to the above-mentioned atomic ond molecular carriers of the negative charge are found on a vertical line. The distance of this line from the vertical line through the origin is nearly equal to the corresponding distance for the positive parabolas. This fact leads us to infer that, as J. J.

[1] $Cl_I = 34$, $Cl_{II} = 36$. See M. Ishino, l. c.

Thomson has suggested, the maximum kinetic energy of these negatively charged particles is equal to that for the corresponding positive ones. The amount of this kinetic energy is determined by the potential difference between the anode and cathode of the discharge-bulb.

The appearance of the negative particles may be explained by the following consideration.

Being once positively charged in front of the cathode, the negative particles acquire their high speed under the action of the intense electric field. After passing through the cathode each of the particles get neutralized, and then capture an electron, and becomes negatively charged. In the case under consideration, the captures of electrons by SO, SO_2 and NO are due to their strong electro-negative behaviour.

(4). The second bead on the parabola due to negatively charged atoms.

In addition to the main bead of a negative parabola, the second one is also sometimes observed on the prolongation of the parabola to the origin. The features are shown in Fig. 1, Fig. 4 and Fig. 5, Plate I, in which are present the lines due to C^-, O^- and S^-. Similar beads also occur in the parabolas of Cl^-_{I}, Cl^-_{II}, which are shown in Fig. 1 in Plate in the paper[1] by one of the authors. The position of the second bead is about midway between the vertical line passing through the first main bead and that through the origin.

The existence of these second beads suggest to us that in the discharge bulb the particles producing the beads possess double positive charges but by passing through the cathode, they lose these and capture one electron.

The prolongation of the negative parabola to the origin is generally so faint, that it was not easy to take the photograph of the second bead. The above mode of explanation is strongly supported by the following facts. When the negative second beads are present, we generally find on the positive side of the same photographic plate the corresponding positive second beads. Besides we find the lines for which the value of $\frac{e}{m}$ is twice that of the second beads. These lines begin from the vertical line for the main beads and they are

1 Loc. Cit.

due to the particles which have still retained their double positive charges after passing through the cathode.

(5). The third bead on the negative parabola.

In Fig. 5 and Fig. 6 in Plate I, it is clearly seen that in the parabolas due to H^-, O^-, Cl^- etc. there are the third beads, the distance of which from the vertical line through the origin being twice that of the main beads of the parabolas. It is a very striking fact that whenever these third beads make appearance, the parabolas due to the corresponding molecules with positive charge always occur associated on the positive side of the plate.

Judging from this we see that the negatively charged particles which produce the above third beads are probably the atoms resulting from the splitting up of the positively charged molecules after passing through the cathode.

(6). The secondary line due to the negatively charged particles.

It is seen in Fig. 5, 6, 7 and 8 in Plate II, that the parabolas due to the atoms of H^-, O^-, Cl^-, S^- are sometimes accompanied by the secondary lines. These lines are, like those in the case of positively charged particles, probably due to the particles which are charged only for a short time while they are travelling in the electric and magnetic fields.

SUMMARY.

We have found some new facts relating to the negatively charged particles in the positive ray tube. Some negatively charged molecules of compounds previously unknown were observed.

Next the second and third beads on the primary negative parabolas were discovered; and finally the secondary lines due to negatively charged particles were found.

In conclusion the author's thanks are due to Professor T. Mizuno for the interest he has taken in this investigation.

Plate I.

Fig. 1.

Parabolas of C_2^-, S^-, SO^-, SO_2^-
Secondary lines of S^-, O^-

Fig. 2.

Parabolas of H_2O^-

Fig. 3

Parabolas of NO^-, O^-.
Secondary line of O^-.

Fig. 4.

Parabolas of Cl_I^-, Cl_{II}^-, O^-, C^-.
Second beads of C^-, O^-, Cl^-.

Plate II.

Fig. 5.

Second beads of O^-, Cl^-.
Third beads of O^-, Cl^-.
Secondary line of O^-.

Fig. 6.

O^-, Cl^-.
The third beads of O^-, Cl^-.
Secondary line of O^-.
Parabolas of H_2O+, $O+$.

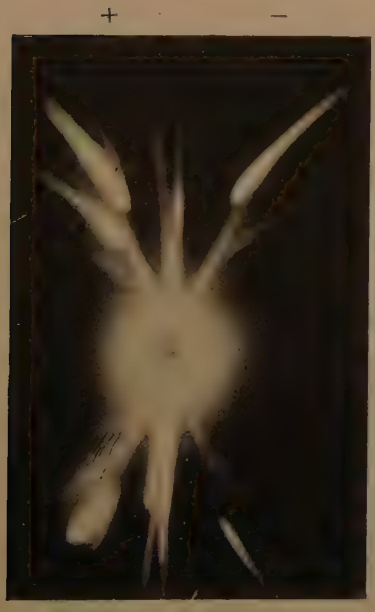


Fig. 7.

Parabolas of O^-, Cl^-.
Third beads of O^-, Cl^-.
Secondary line of O^-.
Parabolas of H_2O+, $O+$.

Fig. 8.

Secondary line of H^-

On the Equilibrium in the System of Copper Sulphate, Ammonium Sulphate, Potassium Sulphate, and Water at 25·0°C.

By

Ryonosuke Hayami.

(Received September 21, 1920).

On the equilibrium in a quaternary system consisting of water and three salts with a common ion, we find not a few laborious works in the literature, most of which are due to J. H. van't Hoff, F. A. H. Schreinemakers, and their co-workers.[1] In certain cases, only the component salts appeared as the residue, while in others some double salts existed also. In the literature, however, there has been reported, so far as the author knows, no case in which a solid solution existed as a residue.

It is well known that, in the systems, $(NH_4)_2SO_4-CuSO_4-H_2O$ and $K_2SO_4-CuSO_4-H_2O$, the double salts, $(NH_4)_2SO_4.CuSO_4.6H_2O$ and $K_2SO_4.CuSO_4.6H_2O$, can respectively exist.[2] Ammonium sulphate and potassium sulphate are completely isomorphous and form solid solutions in all possible proportions, and so are also these double salts. According to A. Fock[3] these two series of solid solutions, single and double salts, give continuous solubility curves of the same type.

1 van't Hoff, Z. anorg. Chem., **47**, 251–253 (1905); Schreinemakers, Z. phys. Chem., **66**, 687 (1909); ibid., **65**, 586 (1909); ibid., **71**, 109 (1919).

2 Schreinemakers and de Baat, Proc. K. Akad. Wetensch Amsterdam, **17**, 533 (1914); J. E. Trevor, Z. phys. Chem., **7**, 469 (1891); Meerburg, J. Chem. Soc., A., II, 380 (1911); Fräulein W. C. de Baat, Z. phys. Chem., **66**, 693 (1909).

3 A. Fock, Z. phys. Chem., **12**. 661 (1893); ibid., **24**, 536, R. (1897); J. Chem. Soc., A. II, 480 (1897); Seidell, Solubilities of Inorganic and Organic Substances, 261, 271.

From these facts we can expect the interesting role which those two series of solid solutions would play in the equilibrium of the system of copper, ammonium, and potassium sulphates and water. Thus, the author took up the study of that system from the standpoint of the phase rule.

Purification of the Materials.

The sulphates of copper, ammonium, and potassium were recrystallised thrice from somewhat acidic, ammoniacal, and neutral solutions respectively of commercial pure salts, washed well with water, and dried. These salts thus prepared were sufficiently pure for the present work.

Methods of Analysis.

The compositions of solutions and residues were determined in the following ways: The total sulphate radical was determined as barium sulphate, of which the precipitation was effected by the cautious addition of the barium chloride or by the rapid method according as the solution was rich in copper or not.

Copper was estimated by the iodometry, using 1/10- and 1/30-normal thiosulphate solutions, which were standardised against iodine purified in the following way: Pure iodine was precipitated from a potassium iodide solution by addition of water, then distilled from water suspension and finally dried in a desiccator containing conc. sulphuric acid.

Ammonia was distilled by the addition of caustic soda into a known volume of normal sulphuric acid, which was then titrated with 2/10-normal carbonate-free caustic soda solution by using methyl orange as indicator.

All the analytical operations were carried out under as much the same conditions as possible throughout the experiment. Potassium and water were estimated by difference.

Methods of Experiments.

In such a quaternary system as that under consideration, when two solid phases exist, the system becomes bivariant and in a given temperature it has only one degree of freedom. At 25° we may

have the following two different cases of this kind of equilibrium, in which the solid phases are respectively:

(A) $CuSO_4.5H_2O$, $CuSO_4.(y(NH_4)_2(1-y)K_2)SO_4.6H_2O$;
(B) $CuSO_4.(y(NH_4)_2(1-y)K_2)SO_4.6H_2O$, $(x(NH_4)_2(1-x)K_2)SO_4$.

For convenience, we designate the solid solutions of the double salts by S_1 and those of the single sulphates by S_2.

The experimental method adopted for case A was as follows:—

In an Erlenmeyer flask of a capacity of about 59 c.c., certain amounts of the potassium and ammonium salts were completely dissolved in water at 60°, and then an excess of finely powdered copper sulphate was added. The flask was made to rotate in a thermostat at 25·0° for at least three days; usually the equilibrium was attained after two days' rotation. Then the flask was left at a stillstand in the same thermostat for a while until the solid phases had settled, when the solution was taken out by a pipette through a cotton filter and divided into six weighing tubes. The residue was separated from the solution and the adhering mother liquor was removed by pressing and rubbing it between folded filter paper as rapidly as possible; then it was dissolved in water to a definite volume.

In this case the residue consisted always of two species of crystals differing in colour and size. The copper sulphate appeared as large deep blue triclinic crystals, the habitus was somewhat columnar, often attaining a size of about 7 mm. It was mechanically separated and on analysis proved to be the pure hydrate, $CuSO_4.5H_2O$. On the other hand, the solid solution consisted of very fine, light blue crystals, which appeared as rhombus forms under the microscope; after removing the copper sulphate crystals they were found to be represented by the formula assigned to the solid solntion S_1. The composition of the solid solution varied continuously with that of the liquid phase.

The experiment for the case B was carried out in a quite different way. In the previous case A, the procedure was very simple, as, though there appeared two solid phases, one of them was only a single salt of a definite composition. Now, in the case B the matter is far more complicated, because the co-existence of two kinds of solid solutions is expected. The preliminary examinations were undertaken as follows:— A comparatively small quantity of copper sulphate, and ammonium and potassium sulphates in different proportions were mixed with water in an Erlenmeyer flask, and the mixture

was made to attain equilibrium at 25·0° as in the other case. The composition of the solutions varied continuously whenever in the residue the copper radical, in the molecular relation, was less than half the total sulphate radical, and there was no indication of the existence of more than two solid phases. In a case when the residue contained the copper radical in a quantity the exact moiety of the total sulphates, the water of crystallization almost satisfied the requirement for the solid solution, S_1. Moreover, when the residue contained a very small quantity of copper, the co-existence of the solid solution, S_2, could be directly confirmed. Both of these solid solutions were very fine crystals discriminated from each other by their rhombus and orthogonal shapes under the microscope, but to the naked eyes the mixture appeared homogeneous.

For the determination of the compositions of these residues, the mutual separation of them for analysis would have given the most accurate and simplest method, but the simple mechanical separation was impossible. The utilization of the difference of a physical property, i.e. the specific gravities of the substances, suggested itself, but preliminary experiments proved the futility of it.

Now as the direct separation of the mixed residue ended in failure, some other method had to be sought. If we get a residue which contains a large quantity of one of the solid solutions and a very small part of the other, we can determine at least approximately the composition of the former, but this is a tedious and speculative method. If we have two kinds of residues which correspond to the one and same solution and yet contain the two solid solutions in different proportions, we can determine the compositions of the two phases at the same time, as we now obtain two equations for two unknown quantities. This method is more interesting and practicable than the above method, and was adopted in the second experiment. This method is based on the following consideration.

The residue (1) consists of a large part of the solid solution S_2 of the single salts and a small part of the other solid solution S_1. The residue (2), on the contrary, contains a relatively very large quantity of the latter. Let the molecular ratio of copper, ammonium, and potassium sulphates in the residue (1) be $a : b : c$, and that in (2) $a' : b' : c'$, then we have the following relations.

In the residue (1) containing 1 mole of copper sulphate, we have

(b/a) = moles of total ammonium sulphate,
$(b/a-y)$ = moles of ammonium sulphate contained in the solid solution S_2,
$(b/a+c/a)$ = moles of total ammonium and potassium sulphates,
$(b/a+c/a-1)$ = moles of ammonium and potassium sulphates forming the solid solution S_2,
$(b/a+c/a-1)x$ = moles of ammonium sulphate in the solid solution S_2,

therefore,

$$(b/a+c/a-1)x = (b/a-y).$$

Similarly for the residue (2), we have

$$(b'/a'+c'/a'-1)x = (b'/a'-y).$$

From these two equations, we have

$$x = (ba'-b'a) / ((b+c)a'-(b'+c')a)$$
$$y = ((c-a)b'-(c'-a')b) / ((b+c)a'-(b'+c')a).$$

In order to diminish errors in the calculation, the residues must have in their compositions as large a difference as possible. For this purpose the experiment was carried out in the following way:— The quantities of the sulphates and water were taken in such proportions that the residue (2) was deposited when they attained the equilibrium state. They were put in a special tube of H-form of about 100 c.c. capacity, and were made to form a solution at 60°, then the tube was set in rotation in the thermostat at 25·0° for about 24 hours. Now, nearly all the residue was collected in one limb of the tube and the solution was divided almost equally between both limbs. By means of a curved glass rod a piece of cleaned cotton cloth of about 5 cm. square was put into the lateral part of the tube in such a manner that it made complete contact with the glass wall. To the limb, where only a small portion of the residue was present, a finely powdered mixture of ammonium and potassium salts, which was roughly calculated to make the residue (1), was added. The H-tube was warmed to dissolve the salts as much as possible, then cooled by shaking it in cold water to have the deposition of the solid solutions,

during these operations care being taken that the contents of the two limbs should not be mixed up. Finally the tube was made to rotate in the thermostat round an axis parallel to the lateral part of the tube. In this way the equilibrium in each of the two parts and also between them was effected without much mixing of residues with each other. At first, however, failures occurred very often, as when a large cloth was inserted, the equilibrium between the two parts was reached very slowly, while if a smaller one was used, the residue in the two parts became mixed up. But by introducing a modifications in the shape of the H-tube, namely by somewhat tapering the lateral tube toward the places where it opens into the side tubes, the difficulty was removed. After three weeks' revolution the solutions and the residues in both limbs were taken out and subjected to analysis. This method gave a satisfactory result as expected from the preliminary experiments, but the error was naturally much higher than in the former case A.

Results.

The results obtained in the experiments for the simple case A are given in the following tables.

TABLE I.

Composition of solution saturated with copper sulphate and solid solution S_1 in gram percentages.

No.	$CuSO_4$	$(NH_4)_2SO_4$	K_2SO_4	H_2O
1	19·32	...	2·82	77·86
2	19·36	0·83	2·58	77·23
3	19·37	1·11	2·66	76 86
4	19·45	1·66	2·12	76·77
5	19·36	2·01	2·11	76·52
6	19·32	2·64	1·92	76·12
7	19·51	2·82	1·69	75·98
8	19·38	3·34	1·44	75·84
9	19·46	3.81	1·04	75·69
10	19·50	4·17	0·85	75·48
11	19·50	4·64	0·63	75·23
12	19·46	4·83	0·48	75·23
13	19·47	5·33	...	75·20

The following table was deduced from these data.

TABLE 2.

In this table the composition of solution is represented by the formula $100mH_2O.XCuSO_4.Y(NH_4)_2SO_4.(100-X-Y)K_2SO_4$.

No.	X.	Y.	(100−X−Y).	m.
1	88·22	...	11·78	31·49
2	85·23	4·41	10·36	30·11
3	83·68	5·82	10·50	29·40
4	83·14	8·56	8·30	29·07
5	81·66	10·22	8.12	28·58
6	79·62	13·15	7·23	27·78
7	79·75	13·93	6·32	27·49
8	87·38	16·30	5·32	27·17
9	77·76	18·41	3·83	26·79
10	77·02	19.89	3·09	26·40
11	75·95	21·81	2·24	25·95
12	75·63	22·68	1·69	25·89
13	75·14	24·86	...	25·70

TABLE 3.

Molecular ratios of sulphates in the residue.

$$CuSO_4 : (NH_4)_2SO_4 : K_2SO_4 = a : b : c$$

No.	a	b	c
1	...	...	...
2	41·37	3·17	25·98
3	45·91	3·67	21·04
4	43·21	7·12	20·86
5	43·67	7·10	14·57
6	38·13	16·38	21·16
7	46·93	12·03	12·61
8	39·87	21·00	15·03
9	42·63	21·97	9·48
10	42·09	26·13	7·68
11	42·43	27·76	4·27
12	41·46	31·96	3·71
13	...	...	...

TABLE 4.

Molar fraction of ammonium sulphate in total alkali sulphates.

No.	In aqueous solution.	In solid solution.
1	...	...
2	29·80	10·88
3	35·56	14·86
4	50·79	25·47
5	55·62	32·74
6	64·51	43·62
7	68·74	48·83
8	75·36	58·29
9	82·85	69·86
10	86·56	77·29
11	90.63	86·68
12	93·05	89·60
13	100·00	100·00

The results for the case B are in the following.

TABLE 5.

Composition of solution saturated with two solid solutions, namely S_1 and S_2, in gram percentages.

No.	$CuSO_4$	$(NH_4)_2SO_4$	K_2SO_4	H_2O
1	1·30	...	11·14	87·56
2	1·35	1·71	11·07	85·87
3	1·35	2·23	10·92	85·50
4	1·36	4·17	10·54	83·93
5	1·34	6·59	10·07	82·00
6	1·35	7·97	10·28	80·40
7	1·27	10·47	9·45	78·81
8	1·20	12·83	8·96	77·01
9	1·08	17·88	8·16	72·88
10	0·92	20·77	7·60	70·71
11	0·89	22·35	7·20	69·56
12	0·82	25·49	6·20	67·49
13	0·64	28·62	5·13	65·61

14	0·55	33·44	4·02	61·99
15	0·43	37·18	3·58	58·81
16	0·40	40·16	2·06	57·38
17	0·37	43·10	...	56·53

TABLE 6.

In this table the composition of solution is represented by the formula $100mH_2O.XCuSO_4.Y(NH_4)_2SO_4.(100-X-Y)K_2SO_4$.

No.	X.	Y.	(100−X−Y).	m.
1	11·27	...	88·73	67·41
2	9·93	15·26	74·81	56·10
3	9·59	19·19	17·22	53·90
4	8·46	31·35	60·19	46·28
5	7·28	43·01	49·76	39·22
6	6·61	47·19	46·20	34·92
7	5·60	56·02	38·38	30·91
8	4·80	62·23	32·97	27·37
9	3·59	71·66	24·75	21·40
10	2·80	76·10	21·10	19·00
11	2·58	78·27	19·15	17·86
12	2·20	82·56	15·24	16·04
13	1·61	86·62	11·77	14·56
14	1·24	90·53	8·23	12·30
15	0·88	92·39	6·73	10·71
16	0·79	95·48	3·73	10·00
17	0·70	99·30	...	9·55

TABLE 7.

Molecular ratios of sulphates in the residues.

No.	a : b : c	a′ : b′ : c′
1	...	...
2	0·28 : 0·54 : 89·98	17·44 : 1·21 : 63·54
3	0·41 : 0·36 : 90·73	19·49 : 1·53 : 69·98
4	0·21 : 0·62 : 90·54	21·68 : 2·32 : 56·41
5	5·33 : 1·80 : 82·06	14·88 : 2·90 : 66·27
6	4·83 : 2·79 : 81·22	16·02 : 4·15 : 63·34
7	6·30 : 4·72 : 79·01	21·57 : 8·26 : 52·52

8	2·98	10·92	77·78	25·65	11·10	42·30
9	2·95	10·06	74·55	30·05	16·54	32·59
10	5·34	18·32	70·55	23·37	20·42	40·93
11	7·62	21·46	64·72	33·56	21·92	23·72
12	6·43	25·84	61·45	35·24	24·39	18·66
13	2·83	31·12	64·07	32·34	36·40	22·42
14	6·84	40·93	49·70	36·53	30·83	12·20
15	3·72	66·83	37·40	37·64	36·24	7·35
16	3·26	83·81	22·63	37·58	36·29	5·29
17	...	...	...	...	...	...

TABLE 8.

Molar fraction of ammonium sulphate in total alkali sulphates.

No.	In aqueous solution	In single solid solution S_2	In double solid solution S^1
1	...	...	...
2	16·93	0·58	5·34
3	21·23	0·37	7·03
4	34·27	0·66	9·55
5	46·34	1·29	14·76
6	50·54	2·42	18·14
7	59·34	3·50	32·03
8	65·39	11·69	30·63
9	74·32	16·84	44·33
10	78·29	18·24	57·71
11	80·35	21·74	57·48
12	84·43	26·93	63·24
13	88·02	31·70	65·49
14	91·64	42·59	76·91
15	93·22	63·30	86·33
16	96·25	78·45	88·28
17	100·00	100·00	100·00

From the data in Tables 2 and 6, neglecting water, Fig. 1 was obtained, and from data in Tables 4 and 8, Fig. 2.

In Fig. 1, the angular points, A, B, and C, represent $CuSO_4$, $(NH_4)_2SO_4$, and K_2SO_4 respectively, and the straight lines, BC and HK, the single solid solutions S_2 and the double solid solutions S_1

respectively. The curves, DE and FG, represent the solutions saturated with $CuSO_4.5H_5O$ and the double solid solutions and those saturated with the double and single solid solutions respectively. The relation between the compositions of the solutions and the residue is expressed by the tie lines connecting the corresponding points.

In Fig. 2, the horizontal and vertical sides represent the molar fraction of ammonium sulphate in the total alkali sulphates in the solid solutions and in the aqueous solutions respectively, and those three curves, representing the three cases respectively, show the relative distribution of the two alkali sulphates between solid and liquid solutions.

Summary.

The equilibrium in the system of copper, potassium, and ammonium sulphates and water at 25°C. has been studied and the relation between the composition of aqueous solutions and that of the solid solutions determined when the residue is a mixture of $CuSO_4.5H_2O$ and $CuSO_4.(NH_4, K)_2SO_4.6H_2O$ and also when it is a mixture of $(NH_4, K)_2SO_4$ and $CuSO_4.(NH_4, K)_2SO_4.6H_2O$.

In the latter case, where the single and double solid solutions are mixed in the residue, it was difficult to determine the compositions of those solid solutions separately. Thus a new experimental method was devised to remove that difficulty, and it proved to be satisfactory.

This work was suggested by Prof. Y. Osaka and carried out under his direction. The author wishes to take this opportunity to thank him for his helpful suggestions and kind instructions.

Fig. 1.

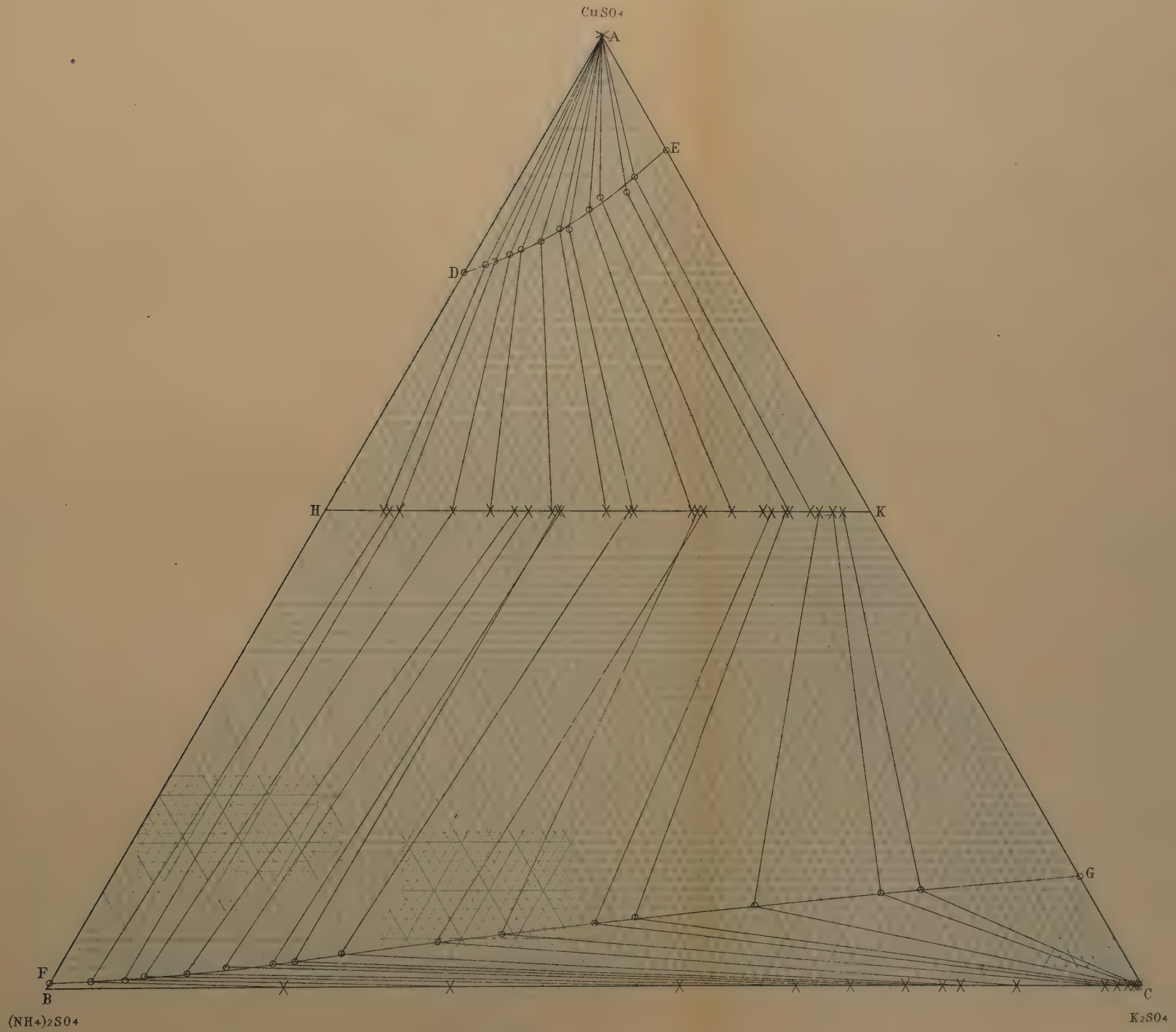
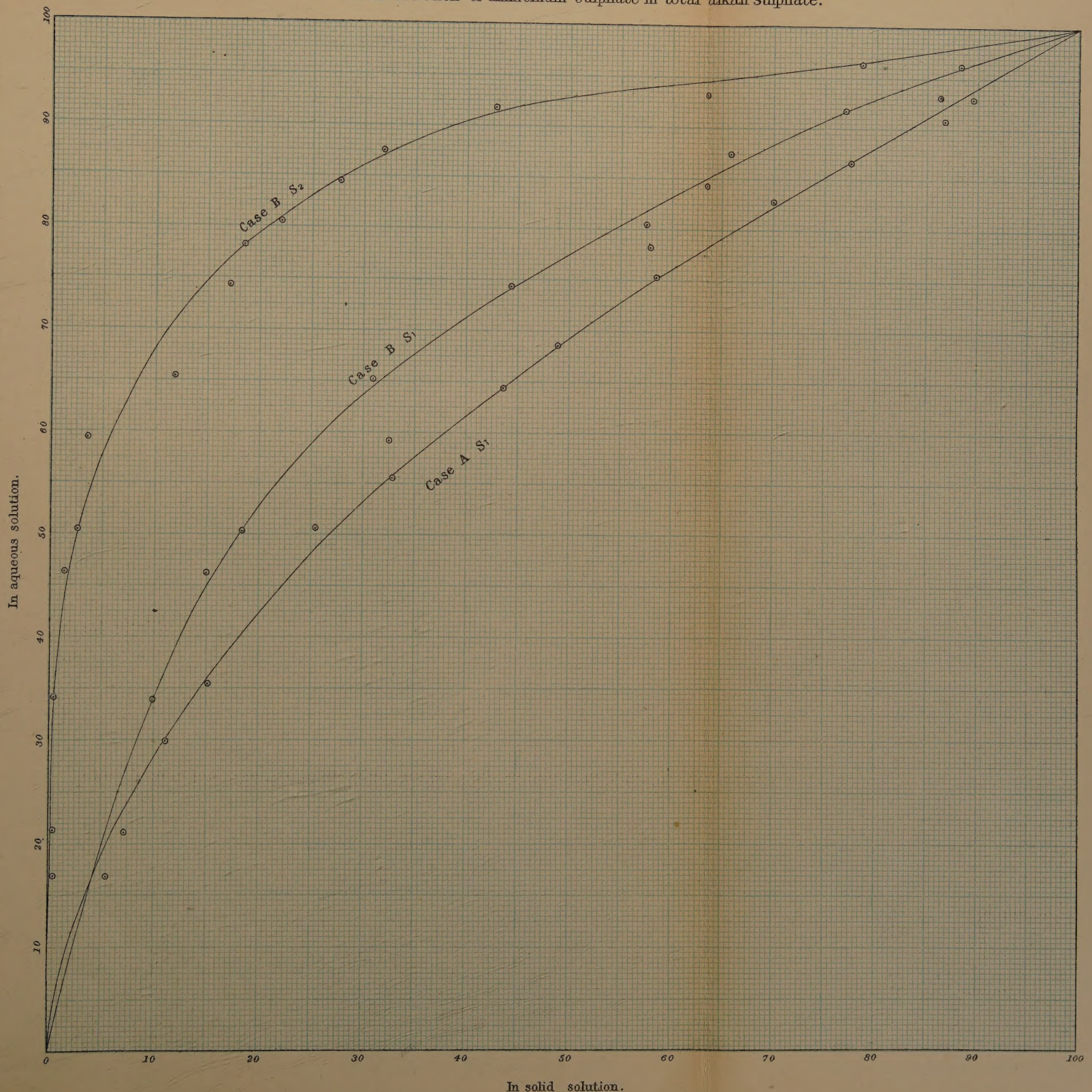


Fig. 2.

Molar fraction of ammonium sulphate in total alkali sulphate.



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